

STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF PEROVSKITE LaCoO_3 AND LaFeO_3 NANO CRYSTALLINE POWDERS

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Abstract

Perovskite based transition metal oxides has been focused since the last few decades because of its wide range of applications in the environmental catalyst, gas sensors, oxygen permeation membranes, electrode materials in solid oxide fuel cells (SOFCs) etc. The aim of the research work is to study the structural, optical and electrical properties of perovskite type LaCoO_3 and LaFeO_3 . These nanocrystalline powders were synthesized by citrate sol-gel method by using metal nitrates as starting materials and citric acid as the chelating agent. The dried precursor powders of LaCoO_3 and LaFeO_3 were amorphous and their thermal decomposition occurs stepwise upon heating to 600 °C by TG-DTA analysis. Pure perovskite type single phase LaCoO_3 and LaFeO_3 powders are formed after heating at 450 °C. The pellets prepared from calcined powders were sintered at 800, 900 and 1000 °C and crystalline pellets were characterized by XRD, FT IR, EDXRF, SEM, UV-Visible spectrometer and LCR meter. The XRD data confirms that the LaCoO_3 has hexagonal structure with space group R3c and LaFeO_3 has orthorhombic structure with space group Pnma. SEM micrograph shows that nanostructure and EDXRF analysis confirms that the all elements of the sample were present in good agreements with stoichiometric ratio. The optical properties of LaCoO_3 and LaFeO_3 were studied from UV-Visible spectrophotometer and the optical band gaps were also estimated by using Tauc's relation. The band gap values of these samples are 2.10eV and 2.40 eV respectively and these values are lie within semiconductor band-gap range. Frequency dependence of dielectric behaviour of the two perovskite samples was examined by LCR meter within the frequency range of 100 kHz- 1000 kHz. Dielectric loss tangent and dielectric loss were found to decrease with increase of frequency. The ac conductivity was dependent on the dielectric nature of the prepared samples and it was gradually increased with increase of frequency. The resistivity of LaCoO_3 sample is lower than that of LaFeO_3 sample. The dc and ac conductivities of LaCoO_3 are higher than that of the LaFeO_3 sample.

Keywords: Perovskite, LaFeO_3 , LaCoO_3 , citrate sol-gel method, optical properties, electrical conductivity

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Introduction

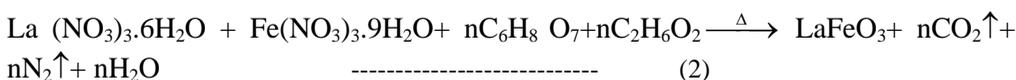
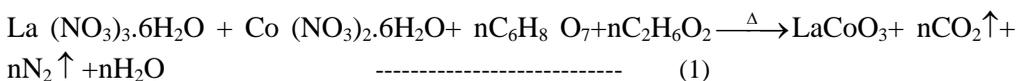
Perovskite is a mixed oxide of transition metals with chemical formula ABO_3 where A is transition metal or lanthanide series cation B is transition metal cation and O is oxide anion. The structure of perovskite is a face-centered cubic cell of cation A and anion O. In the unit cell, cation A locates at the cubic corner and B at the center of the lattice. Several properties such as structure, electronics and magnetics of these compounds depend on the type of cations A and B. The property and use must be considered hand in hand, for example the perovskite for use as gas sensor should have A and B such that ABO_3 exhibits electronic property as semiconductor or if the aim is in fuel cell the selected ABO_3 should have dielectric (K) property. The La-based perovskite of $LaCoO_3$ and $LaFeO_3$ are very interesting compounds and their application can be found in many fields (Haron *et al.*, 2016). The $LaCoO_3$ find application in the field of catalyst, fuel cell and gas sensor while the $LaFeO_3$ perovskite have been studied as photocatalyst, gas sensor and cathode for fuel cell (Haron *et al.*, 2016). The efficiency of these materials depends on the synthesis methods. Many methods are available for the synthesis of perovskite oxide in the group of La-based perovskite such as solid state reaction, sol-gel method, solution combustion synthesis, hydrothermal synthesis and co-precipitation method etc. (Unikoth *et al.*, 2014). In this paper, $LaCoO_3$ and $LaFeO_3$ nanocrystalline samples were synthesized via a simple citrate sol-gel method and their structural, optical and electrical properties were investigated for further applications. This synthesis route has several advantages such as simplicity, low cost and no waste compared with other methods.

Materials and Methods

Synthesis of Perovskite $LaCoO_3$ and $LaFeO_3$ Powder

Perovskite $LaCoO_3$ and $LaFeO_3$ nanocrystallite powders were prepared with some based modification on the citrate sol-gel method. All chemicals were analytical grade and used without further purification. They were procured from the British Drug House Chemical Ltd., England (BDH). The deionized water was used throughout the experiment. $La(NO_3)_3 \cdot 6H_2O$ and

Co (NO₃)₂.6H₂O were used as starting materials for preparation of LaCoO₃. A specific amount of each salt was dissolved in deionized water and mixed together with vigorous stirring. And then citric acid solution was added in the mixture solution. Citric acid that was equivalent in gram mole with that of total cations (La³⁺, Co²⁺) (Anupama and Prasad, 2015). Subsequently, 5 mL of ethylene glycol was added to the mixture solution. Resulting purplecoloured solution was heated at 80 °C under continuous stirring. After being heated for about 6 h, the resulting solution became highly viscous and the purple transparent gel was formed. Finally, the xerogel was obtained after the gel was dried completely in an oven at 120 °C for 6 h. The xerogel was ground in the mortar and pestle (Khetre *et al.*, 2010). The xerogeldried powder was calcined at 400 °C, 450 °C and 500 °C each for 4 h. The resulting calcined powders were compacted in a mortar driven uniaxial hydraulic press, using a mold 10 mm in diameter. The pellets thus obtained were sintered at 800, 900 and 1000 °C for 4 h. For perovskite LaFeO₃, the same procedure as above was applied but with Fe (NO₃)₃.9H₂O as starting material. The citrate sol-gel synthesis occurs according to the following overall reaction (1) and (2) which give rise to perovskite powders and gaseous species.



Characterization of the Prepared Perovskite LaCoO₃ and LaFeO₃

The thermal decomposition behaviours of the powders prepared by citrate sol-gel method were characterized by thermogravimetric and differential thermal analysis (TG-DTA) at a heating rate of 10°C/min in nitrogen. The phase identification of the as-prepared powder was performed using X-ray diffractometer with CuK_α radiation (λ = 1.5405 Å). The lattice parameters and the average crystallite size were calculated using PDXL-software. The crystallite size was also compared with the values obtained using Debye-Scherrer formula, $D = 0.9 \lambda / \beta \cos\theta$, where λ is X-ray wavelength and β is peak width at half maximum. The FTIR measurements have been performed in the region of 400- 4000 cm⁻¹ by using 8400

SHIMADZU, Japan FT IR spectrometer. The elemental compositions of LaCoO_3 and LaFeO_3 perovskite oxides prepared by citrate sol-gel method were investigated by using energy dispersive X-ray fluorescence spectrometer (EDXRF). The morphology of the prepared nano powders was characterized by scanning electron microscopy (SEM). The samples were characterized by UV-visible spectrophotometer (SHIMADZU UV-1800) for wavelength dependence absorption spectrum. The frequency dependence dielectric behavior was examined by LCR meter (GWInstek LCR- 8110 G).

Results and Discussions

The perovskite LaCoO_3 and LaFeO_3 were prepared by citrate sol-gel method. The precursor powders of two perovskite were calcined at different temperature 400, 450 and 500 °C for 4 h. The resulting calcined powders were compacted at 5 ton pressure in a motor driven uniaxial hydraulic press, using a mold 10 mm in diameter. The pellets were sintered at 800, 900 and 1000 °C for 4 h. Phase formation began at 450 °C and complete phase pure perovskite material was obtained on sintering the powders at 800, 900 and 1000 °C for 4h. The two perovskite samples were characterized by TG-DTA, XRD, FT IR, EDXRF and SEM analysis. The optimum sintering temperature was 900 °C and the average crystallite size was found 40.93 nm. The optical properties of perovskite LaCoO_3 and LaFeO_3 at 900 °C were studied by UV-visible absorption spectroscopy. Frequency dependence dielectric behavior of the pellet samples were determined by LCR meter.

Thermal Analyses

Thermal analysis can be utilized to identify the thermal stability and the decomposition temperature of the prepared perovskite. Figure 1 shows the TG-DTA thermogram of dried LaCoO_3 xerogel powder. It was observed that two exothermic peaks at 170 °C and 412 °C formed in TG-DTA thermogram. The two exothermic peaks related to the combustion of organic residues and decomposition of metal nitrates due to the formation of expected perovskite LaCoO_3 . It was found that the losses in weight were 12.49 % and 69.10 %. Above 450°C, there was no significant peak and the compound was thermally stable. Figure 2 shows the TG-DTA thermogram of dried LaFeO_3 xerogel powder. There were three exothermic peaks 261°C, 365°C and 408°C observed

in the thermogram. The three exothermic lines related to the decomposition of metal nitrates, combustion of organic chelating and gelating agent, respectively, due to the formation of expected perovskite LaFeO_3 . It was found that the weight losses percent were 35.75 %, 27.66 % and 17.30 %. Above 450°C , it was observed that there was no significant peak and the compound was thermally stable. From above results, it was concluded that the phase formation of LaFeO_3 and LaCoO_3 started at around 450°C .

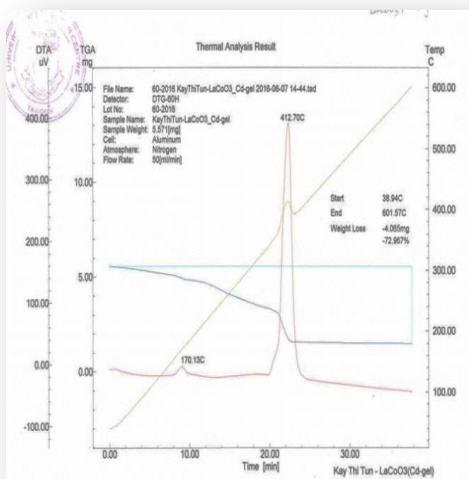


Figure 1: TG-DTA curve of the xerogel LaCoO_3 powder

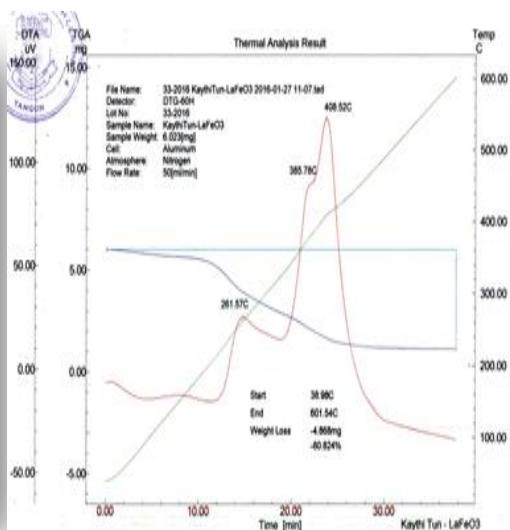


Figure 2: TG-DTA curve of the xerogel LaFeO_3

XRD Analysis

From XRD analysis, the formation of perovskite phase was evidenced in the prepared samples of LaCoO_3 and LaFeO_3 obtained at various temperatures as shown in Figures 3(a-b) and 4(a-b). For LaCoO_3 , the amorphous nature was found at calcination temperature 400°C . The crystalline nature of LaCoO_3 nanoparticles was found at calcination temperatures of 450°C and 500°C and the crystallite sizes of LaCoO_3 found to be 19.37 nm and 26.08 nm respectively. The mixture of La_2O_3 and Co_2O_3 was obtained if the sintering temperature was lower than 900°C . The hexagonal LaCoO_3 perovskite formed at 900°C (matched with ICDD file no.

00-048-01231) and the crystalline size was 40.93 nm. For LaFeO_3 , the amorphous nature was found at the calcination temperature at 400°C and the crystalline nature of LaFeO_3 nanoparticles was found at 450°C and 500°C . The crystalline size of LaFeO_3 found to be 27.87 nm and 28.92 nm, respectively. The effect of variation of sintering temperature on LaFeO_3 is shown in Figure 4(b). All of the peaks can be indexed to be LaFeO_3 structure of orthorhombic due to the lattice parameters agreement with literature. The product obtained from sintering temperatures at 800°C , 900°C and 1000°C was orthorhombic perovskite LaFeO_3 (matched with ICDD file no.00-015-0148) with crystallite sizes of 51.28 nm, 49.76 nm and 66.73 nm respectively. It shows a trend that the average crystallite size is larger at higher calcination temperature, which is related to the grain growth (Theingi, 2013). The resultant data are presented in Table 1.

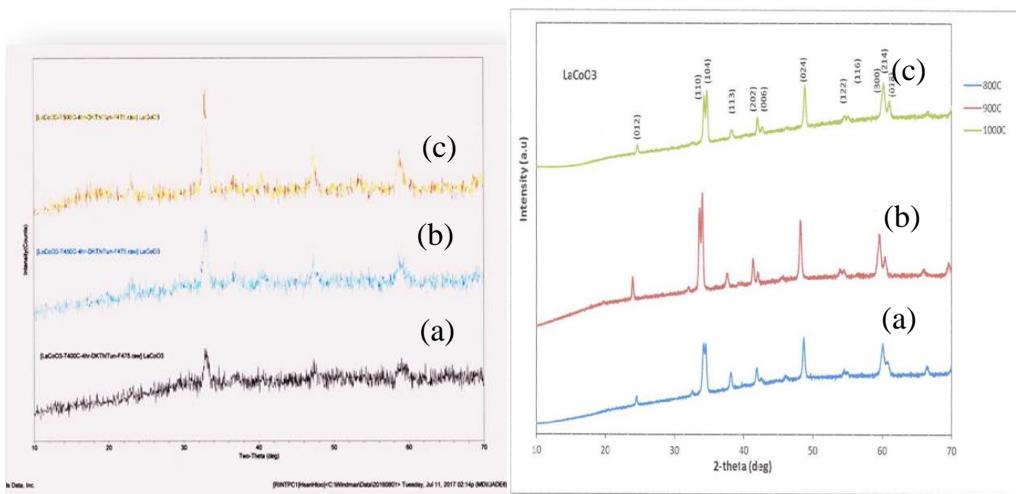


Figure 3:(a)XRD diffraction patterns of LaCoO_3 powder at different calcined temperatures(a) 400°C (b) 450°C (c) 500°C

Figure 3: (b) XRD diffraction patterns of LaCoO_3 samples at sintered 4 temperatures at (a) 800°C (b) 900°C (c) 1000°C

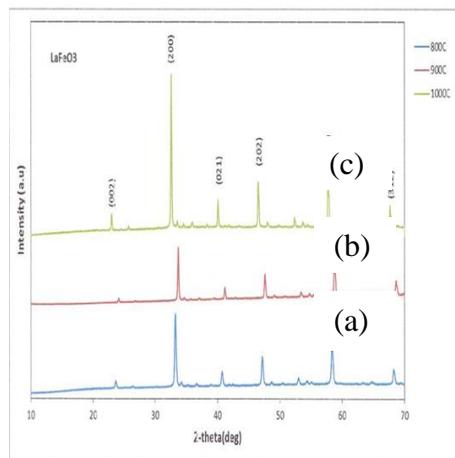
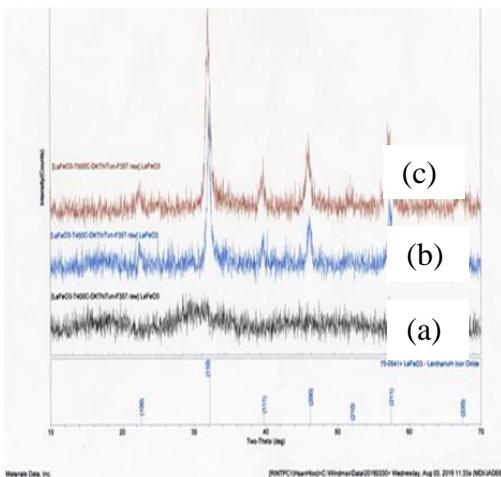


Figure 4: (a) XRD diffraction patterns of LaFeO₃ powder at different calcined temperatures (a) 400 °C (b) 450 °C (c) 500 °C

Figure 4: (b) XRD diffraction patterns of LaFeO₃ samples at sintered temperatures (a) 800 °C (b) 900 °C (c) 1000 °C

Table 1: Crystallite Size of LaCoO₃ and LaFeO₃ Nanoparticles Prepared by Citrate Sol-gel Method

Sample	Temperature (°C)	Crystallite size/D (nm)
LaCoO ₃	450	19.37
	800	17.08
	900	40.93
	1000	37.17
LaFeO ₃	450	27.68
	800	51.28
	900	49.76
	1000	66.73

FTIR Analysis

The LaCoO₃ and LaFeO₃ nanopowder were mixed with appropriate amount of KBr salts to form pellets in order to observe FT IR spectra. FT IR spectra with wavenumber ranged from 400 – 4000 cm⁻¹ are shown in Figures 5 and 6 for LaCoO₃ and LaFeO₃ prepared by citrate sol-gel method,

respectively. Both perovskites LaCoO_3 and LaFeO_3 showed an intense band around 550 cm^{-1} and 417 cm^{-1} due to metal-oxygen stretching vibration group and stretching vibration of La-O group. The low intense peak observed in LaFeO_3 at 3421 cm^{-1} and 1629 cm^{-1} are respectively due to the stretching vibration and bending vibration of O-H group in water molecules. But the hydroxyl group band was not observed in the FT IR data of LaCoO_3 (Ghosh and Dasgupta, 2010).

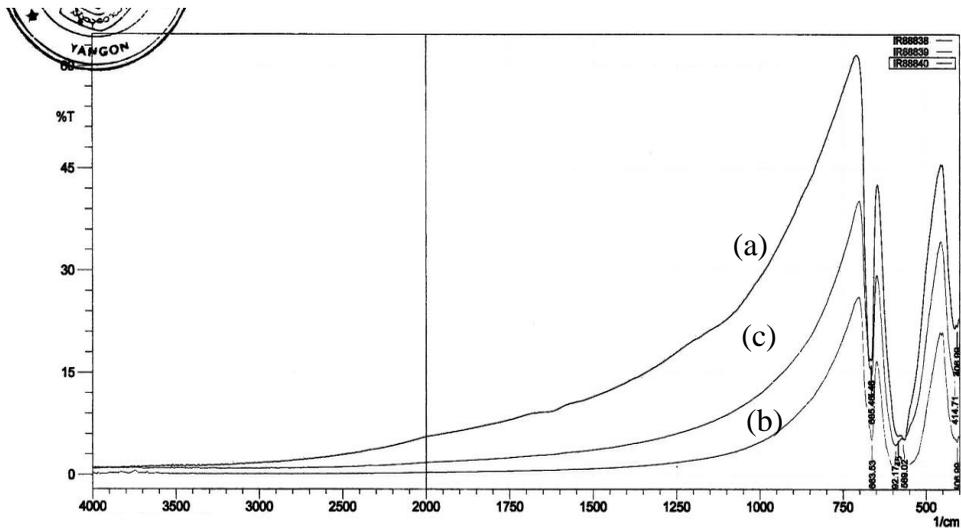


Figure 5: FT IR spectra of LaCoO_3 nanopowder synthesized by sintering at (a) 800°C (b) 900°C (c) 1000°C for 4 h

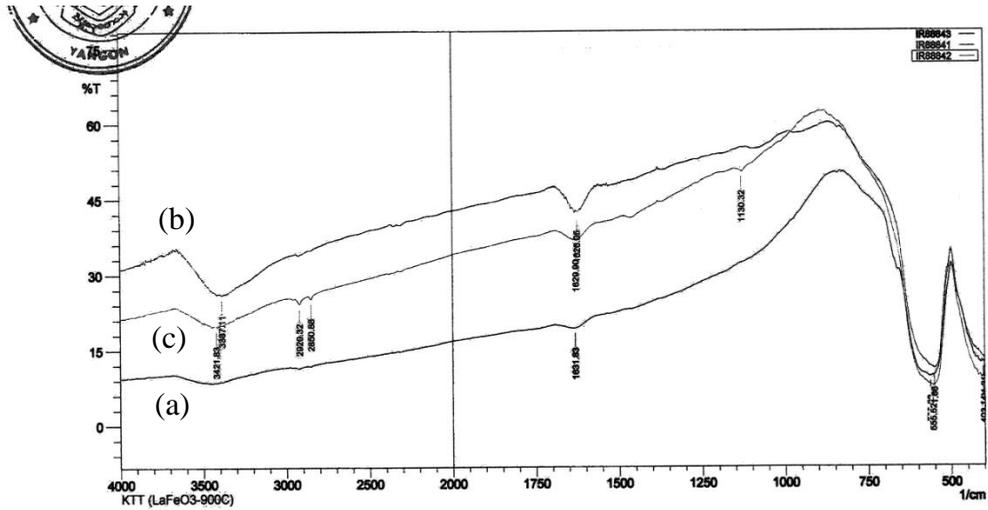


Figure 6: FT IR spectra of LaFeO₃ nanopowder synthesized by sintering at (a) 800 °C (b) 900 °C (c) 1000 °C for 4 h

EDXRF Analyses

The purity of all samples was also determined by using EDXRF analysis. From the EDXRF pattern (Figures 7 and 8), all the elements detected were those that were expected to be present in the sample i.e., La, Co and Fe. In addition, all powder samples contain insignificant amounts of other contaminating elements. On the basis of the relative abundance in the matrix of the samples, the samples contain high percentage of La, Co and Fe. These results confirmed the high purity of synthesized perovskite oxides.

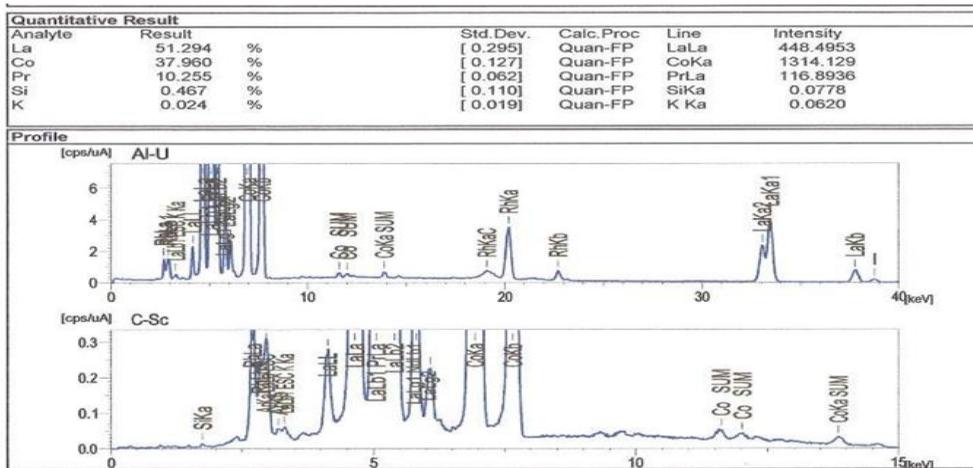


Figure7: EDXRF spectrum of LaCoO_3 nanopowder synthesized by calcined at 450°C for 4 h

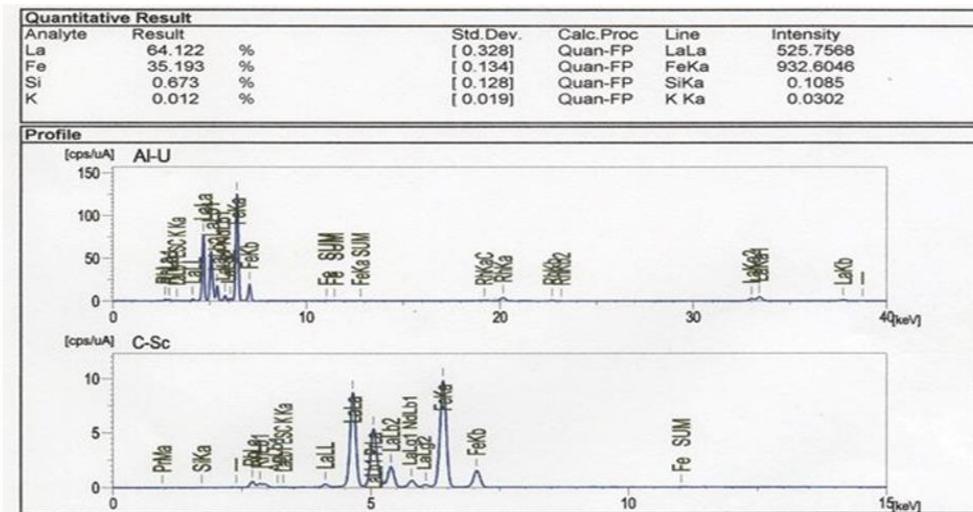


Figure 8: EDXRF spectrum of LaFeO_3 nanopowder synthesized by calcined at 450°C for 4 h

SEM Analysis

The morphology of two perovskite samples was studied by using scanning electron microscope (SEM) with a magnification of 5500 times. Figure 9 and 10 show the SEM micrographs of the perovskite LaCoO_3 and

LaFeO₃. The highly dense structure was seen in perovskite LaCoO₃ and LaFeO₃ samples sintered at 900°C for 4 h. Adjusting the sintering temperature improves the microstructure and the electronic conductivity. It can be seen that each sample has its own characteristic morphology (Haron *et al.*, 2016). The particles morphology of LaCoO₃ was micron size with high degree of agglomeration composed of nanocrystallites with an average size of 40.93 nm at 900 °C (Ghasdi *et al.*, 2010). The microstructure of LaFeO₃ powders were composed of small sized of grains with round shape and crystallite size was 49.76 nm at 900 °C.

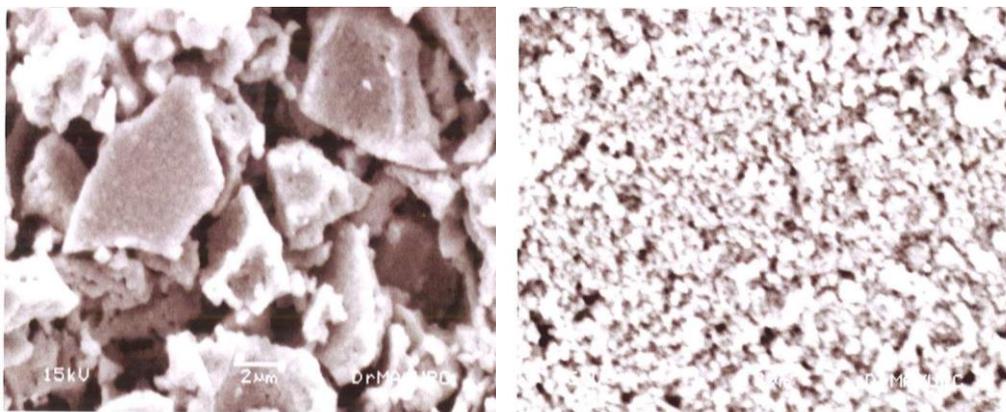


Figure 9: SEM micrograph of LaCoO₃ sintered at temperature 900 °C for 4 h **Figure10:** SEM micrograph of LaFeO₃ sintered at temperature 900 °C for 4h

UV- Vis Spectroscopic Study

UV-visible absorption spectroscopic method is a powerful technique to explore the optical properties of semiconducting nanoparticles. The optical properties of perovskite LaCoO₃ and LaFeO₃ at 900 °C were studied by UV-Visible absorption spectroscopy in the range of 300-700 nm. The absorption coefficient (α) was calculated from the observed absorption spectra and the optical band gap of LaCoO₃ and LaFeO₃ were calculated from the Tauc's plots of $(\alpha h\nu)^2$ vs $h\nu$. Figures 11 and 12 show that the optical band gap of LaCoO₃ was found to be 2.15 eV and LaFeO₃ was found to be 2.40 eV. Band gap values of LaFeO₃ are larger than that of the LaCoO₃. These band gap values are also reliable within the semiconductor band gap ranges. The prepared

materials can be therefore used as gas sensor, cathode material for solid oxide fuel cell, solar cell and other optoelectronic devices.

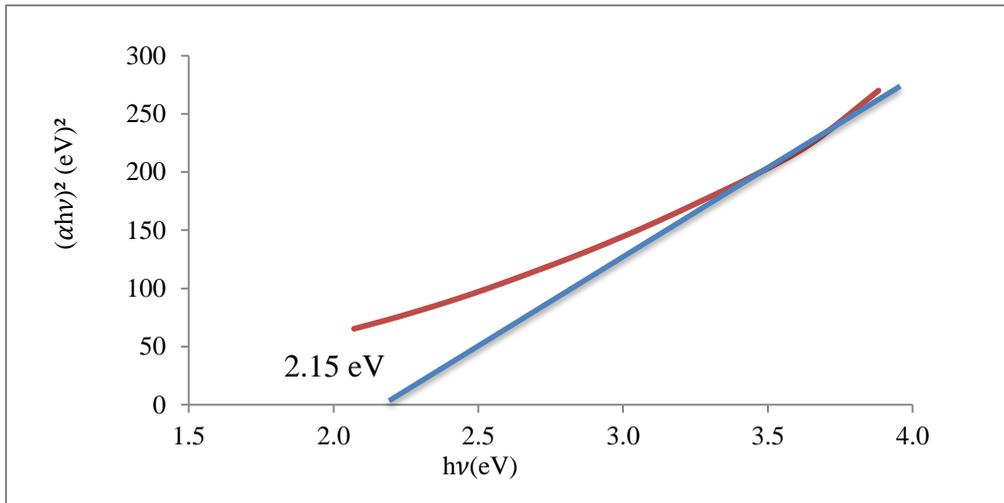


Figure 11: Plot of $(\alpha h\nu)^2$ against $h\nu$ for LaCoO₃ prepared by citrate sol-gel method at 900 °C

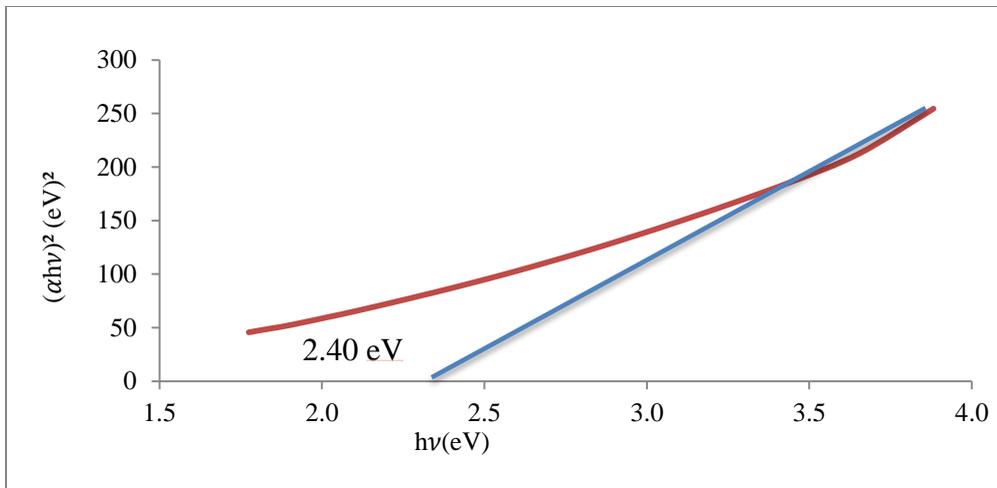


Figure 12: Plot of $(\alpha h\nu)^2$ against $h\nu$ for LaFeO₃ prepared by citrate sol-gel method at 900 °C

Dielectric Studies

Dielectric measurements as a function of frequency in the range of 100-1000 kHz were performed by using LCR meter. The dielectric constant was calculated by using the formula $K = Cd/\epsilon_0 A$ where C is the capacitance of pellet in μF , d is the thickness of the pellet; A is the cross sectional area of the flat surface of the pellet and ϵ_0 is the permittivity for free space. The ac conductivity (σ_{ac}) is obtained from the data of dielectric constant (ϵ_0) and loss tangent ($\tan\delta$) using the relation of $\sigma_{ac} = \epsilon' \epsilon_0 \omega \tan\delta$ where ω ($2\pi f$) is the angular frequency. Thus σ_{ac} depends strongly on the frequency of the applied field (Priyanka *et al.*, 2013). Figure 13(a) and (b) show that dielectric loss tangent ($\tan \delta$) and the dielectric constant decrease with frequency, which is a general ferroelectric behaviour (Unikoth *et al.*, 2014). The higher value of dielectric constant measured at low frequencies can also be explained on the basis of interfacial space charge polarization due to inhomogeneous dielectric structure. The dielectric loss indicates the energy dissipation in the dielectric system (Asad Ali *et al.*, 2015). The lower dielectric constant was found at higher frequencies in LaCoO_3 and LaFeO_3 perovskite samples. The frequency dependence of ac conductivity of LaCoO_3 and LaFeO_3 is shown in Figure 13(c). It can be seen that the conductivity increases with increase in frequency. The resistivity of LaCoO_3 is lower than that of LaFeO_3 sample as shown in Figure 13(d). On the other hand, the higher dc conductivity was found for LaCoO_3 sample than the LaFeO_3 sample as shown in Figure 13(e). There is a correlation between the conductivity and the dielectric behaviour of the material. The conductivity is mainly due to the hopping of electrons and the decreasing function of frequency in the case of band conduction (Priyanka *et al.*, 2013).

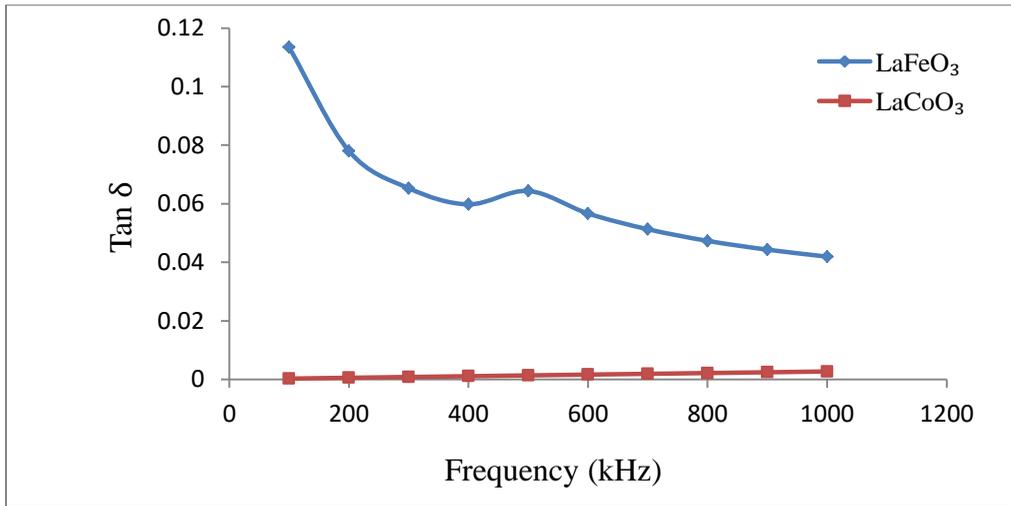


Figure 13:(a) Changes of dielectric loss tangent ($\tan \delta$) of LaCoO_3 and LaFeO_3 as a function of frequency at 2V

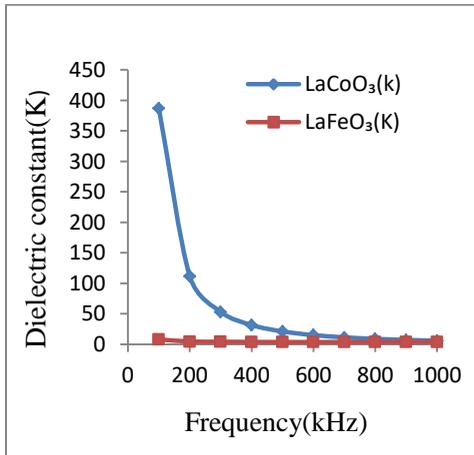


Figure 13:(b). Changes of dielectric constant of LaCoO_3 and LaFeO_3 as a function of frequency at 2V

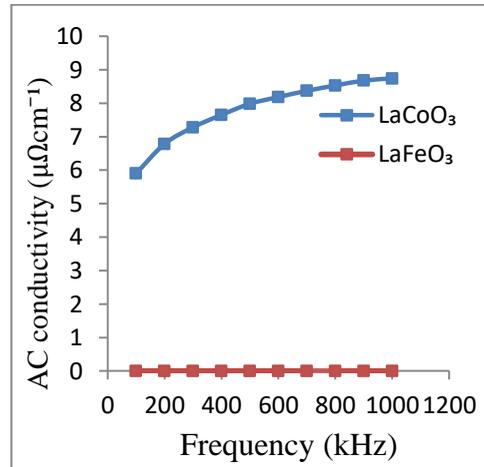


Figure 13: (c). Changes of ac conductivity of LaCoO_3 and LaFeO_3 as a function of frequency at 2V

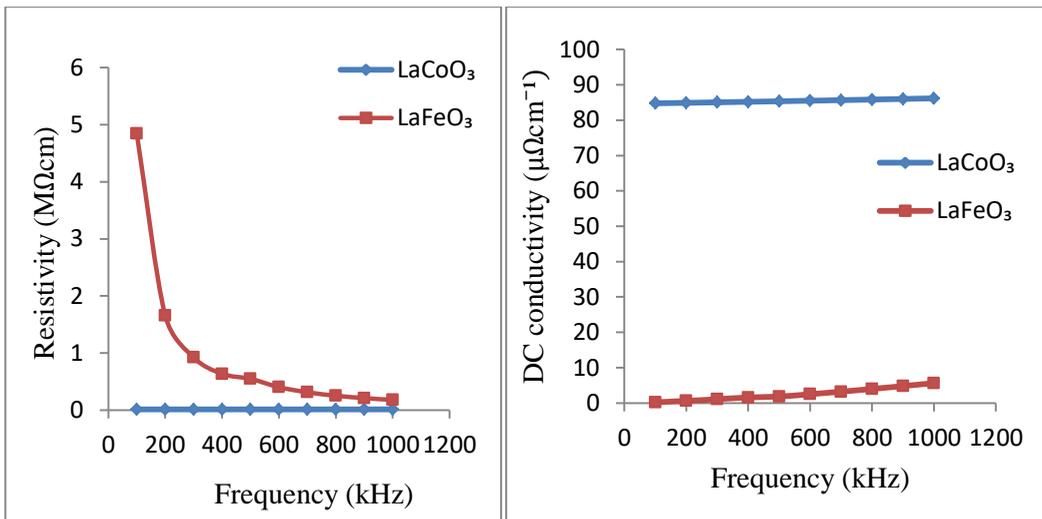


Figure13: (d). Changes of resistivity of LaCoO₃ and LaFeO₃ as a function of frequency at 2V

Figure13:(e).Changes of dc conductivity of LaCoO₃ and LaFeO₃ as a function of frequency at 2V

Conclusion

Perovskite LaCoO₃ and LaFeO₃ samples have been successfully prepared by citrate sol-gel method. The crystalline pellets were obtained by sintering at 900 °C and its structural, optical and electrical properties were studied. From the study of structural properties showed that the LaCoO₃ has hexagonal crystal symmetry with R-3c space group having crystallite size of 40.93 nm and the LaFeO₃ has orthorhombic crystal symmetry with Pnma space group having crystallite size of 40.96 nm. The SEM image showed the nanostructure of the two samples and EDXRF spectra showed the presence of La, Co and Fe. From FT IR analysis, the Co-O and Fe-O stretching vibration mode band are observed at 550cm⁻¹. The band gap was calculated from UV-visible spectra which indicated the semiconducting nature of the materials. The optical band gap of LaCoO₃ and LaFeO₃ were found to be 2.15 eV and 2.40 eV respectively. The ac conductivity and dielectric properties of LaCoO₃ and LaFeO₃ perovskite samples were studied at the frequency range of 100-1000 kHz. The dielectric constant decreased in all samples with increase of frequency. The ac conductivity was high for higher frequencies at a given

temperature. The conductivity of perovskite LaCoO_3 sample have greater than the LaFeO_3 sample.

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