ELECTRICAL AND OPTICAL PROPERTIES OF $LaCo_{0.6}Fe_{0.4}O_3$ NANOCRYSTALLINE POWDER BY SOL-GEL METHOD

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Abstract

A facile transition metal Fe doping has been employed as an effective approach to alter the electrical and optical properties of $LaCoO_3$. The aim of the research work is to study the effect of sintering temperature on structure, electrical and optical properties of the nanocrystalline ceramics. $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline ceramics was prepared from constituent metal nitrates, citric acid and ethylene glycol by sol-gel method and sintered at different temperatures. The $LaCo_{0.6}Fe_{0.4}O_3$ powder calcined at 600 ºC were made circular pellets. The pellets were sintered at 800 ºC, 900 ºC and 1000 ºC. The obtained ceramic pellet samples were characterized by X-Ray Diffractometer (XRD), Fourier Transform Infra-Red (FT IR) spectrometer and Scanning Electron Microscopy (SEM). The XRD results show all $LaCo_{0.6}Fe_{0.4}O_3$ samples have hexagonal crystalline structure with R-3c space group and show single phase. The average crystallite size of the pellet samples varied from 20 to 40 nm due to the growth of nanocrystals at higher temperatures. The respective metal-oxygen stretching vibrations of the prepared samples were observed in FT IR spectra. Surface morphology of the prepared ceramics were studied by SEM. The optical properties of $LaCo_{0.6}Fe_{0.4}O_3$ ceramic samples were studied from UV-visible spectrophotometer and the optical band gaps were also estimated by using Tauc's relation. The band gap values of the pellet samples were 2.2 eV, 2.1 eV and 2.0 eV, respectively and these values were within semiconductor band-gap range. The ac conductivities and dielectric properties were studied by LCR meter in the frequency range of 1MHz - 2MHz. The experimental results indicated that the dielectric loss factor (tan δ), dielectric constant (ε′), ac conductivity (σ_{ac}), resistivity (ρ) and dc conductivity (σ_{dc}) were found to depend on the frequency.

Keywords: $LaCo_{0.6}Fe_{0.4}O_3$, nanocrystalline ceramics, sol-gel method, optical properties

Introduction

Perovskite is 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 (Farhadi and Sepahvand, 2010). $LaCoO_3$-base material has interesting electrical and electrocatalytic properties owing to their high electronic/ionic conductivity. Lanthanum cobaltite, $LaCoO_3$, belongs to a family of mixed electronic and oxide-ion conducting perovskites that are good materials for catalysts, oxygen separation membranes, solid oxide fuel cell cathodes, and oxygen sensors. Cobalt containing perovskite type oxides have received great attention due to their interesting application properties (Moghadam *et al*., 2012).

Cobalt oxide is well known nanomaterial with enhanced electrocatalytic properties for the development of sensitive, efficient, and effective sensors. The electrochemical properties of cobalt oxide are depending on several parameters such as particle dimension surface morphology and tailored electrocatalytic features. Doping of metal oxide nanostructures with particular element offers a novel way for improving the structural, electrical and optical properties. The doping of transition metals is highly used for various oxides such as Cr, Mn, Fe, Ni and Cu that has shown significant change in the structural and optical properties of metal oxide. Iron (Fe) is one of the doping elements that has tremendous chemical stability and is considered important doping element for the enhancement and tuning the structural properties of cobalt oxide (Tahari *et al*., 2016).

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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:

$$t = \frac{rA+rO}{\sqrt{2}\,(rB+rO)} \quad (r_{A(la)} = 1.16\text{Å}, r_{B(Co)} = 0.65\text{Å}, r_{B(Fe)} = 0.55\text{Å}, r_O = 1.35\text{Å})$$

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).

In the present work $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline powder was prepared by citrate sol-gel method. These material have been prepared by many techniques which includes mechanical-synthesis, co-precipitation, solution combustion or thermal decomposition, solid-state reactions, hydrothermal and sol-gel methods. In this paper, $LaCo_{0.6}Fe_{0.4}O_3$ 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

All of the chemicals used were analytical grade. $La(NO_3)_3.6H_2O$ was purchased from Aladdin Industrial Corporation Co., Ltd, Shanghai, China. $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$ and citric acid were purchased from Alpha Chemika Co., Ltd, India. Ethylene glycol was purchased from VMP Chemistry Kontor GmbH Co., Ltd, Germany.

Preparation of Nanocrystalline Powders

$LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline ceramics were 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 lanthanum nitrate (4.32 g), cobalt nitrate (1.74 g), iron nitrate (1.61 g), citric acid (8.4 g) 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 (6.7 mL) 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. The xerogel was ground in the mortar and pestle. The dried xerogel was calcined at 600 ºC for 4 h. The resulting calcined powders were compacted in a mortar driven uniaxial hydraulic press, using a mould with 10 mm in diameter. The pellet ceramics thus obtained were sintered at 800, 900 and 1000°C for 1 h (Derakhshi *et al*., 2016).

Characterization Techniques

Crystal structure and phase analysis of prepared ceramics were performed by X-ray diffraction (XRD) using XRD-2000 diffractometer, Enraf Nonius Co., Bohemia NY, Physics Department, Yangon University. Morphology of the samples 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 samples were characterized by UV-visible spectrophotometer (SHIMADZU UV-1800) for wavelength dependence absorption spectrum. The electrical properties of the prepared samples were studied by using LCR (Inductance, capacitance and resistance) meter.

Measurement of Electrical Properties

Dielectric properties were studied by LCR meter in the frequency range of 1MHz-2MHz. The ac conductivity was calculated from dielectric data using the following relation.

$$\sigma_{ac} = \varepsilon' \tan\delta \omega \varepsilon_o$$

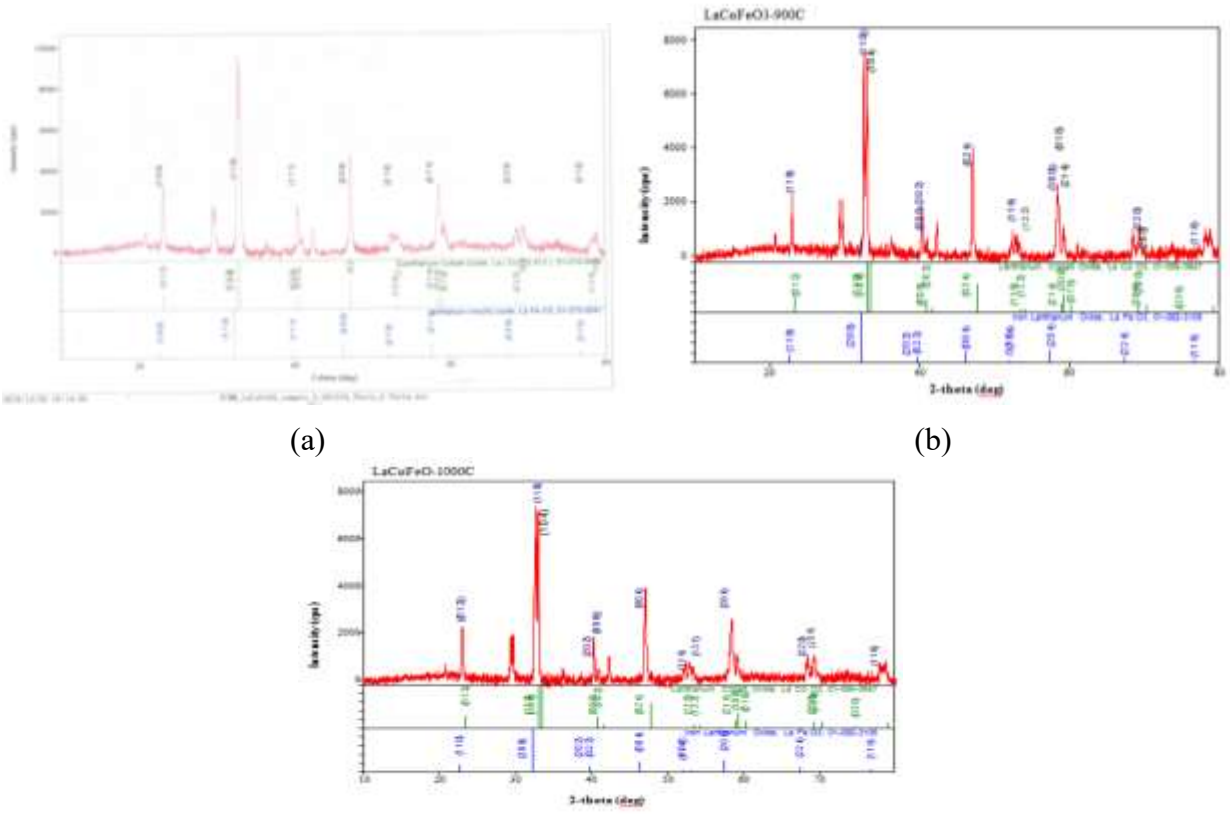
Where σ_{ac} is ac conductivity of the sample, ε' is the dielectric constant, tan δ is the dielectric loss factor, ω is the angular frequency and ε_o is permittivity of free space.

Results and Discussions

Characterization of the $LaCo_{0.6}Fe_{0.4}O_3$ Prepared Samples

XRD analysis

The XRD patterns of the prepared $LaCo_{0.6}Fe_{0.4}O_3$ ceramic sintered at 800 ºC, 900 ºC and 1000 ºC are shown in Figure 1 and their lattice parameters and average crystallite sizes are summarized in Table 1. It was observed that with an increase in the calcination temperature, the intensity of the peak increased. The crystallite sizes of $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline ceramics sintered at 800 ºC, 900 ºC and 1000 ºC were 25.7 nm, 27.6 nm and 32.5 nm, respectively. The diffraction peaks of $LaCoFeO_3$ sintered at 1000ºC, are sharper than those at 800 ºC and 900 ºC. The XRD pattern of each ceramic displayed the reflections corresponding to the trigonal structure of space group hexagonal (R-3c) perovskite $LaCoO_3$ (JCPDS 01-086-1662) and orthorhombic structure of space group Pnma (62) $LaFeO_3$ (JCPDS 00-015-0148). The average particle size of $LaCoFeO_3$ ceramics were found in the range of 20-40 nm. The crystal structure of the prepare samples were matched with those calculated from tolerance factor and they were found to have hexagonal crystal structure.



(a) (b)

(c)

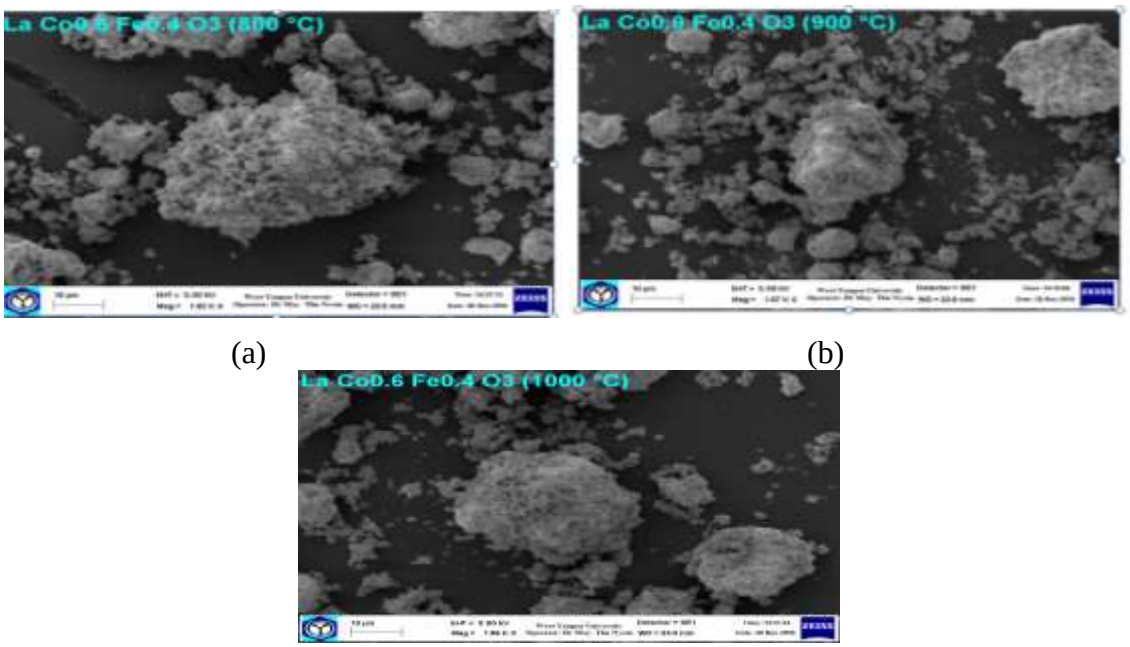
Figure 1 XRD patterns of $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline ceramics sintered at (a) 800 ºC (b) 900 ºC and (c) 1000 ºC

Table 1 Lattice Parameters (a and c) and the Average Crystallite Size of $LaCo_{0.6}Fe_{0.4}O_3$ Nanocrystalline Ceramics Sintered at Different Temperatures

Temperature (ºC)	Lattice parameter (Å)		Crystal system (XRD)	Crystallite size (nm)
	a	c		
800	5.4740	13.204	Hexagonal	25.7
900	5.4208	13.199	Hexagonal	27.6
1000	5.4811	13.210	Hexagonal	32.5

SEM analysis

SEM micrographs of prepared $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline ceramics with different sintering temperatures (800 ºC, 900 ºC and 1000 ºC) for 1 h are shown in Figure 2. As the sintering temperature of $LaCo_{0.6}Fe_{0.4}O_3$ sample increased, the particle sizes were found to become increase and tightly stacked. The compact and dense nature was found at higher temperature the porosity decreased. The high porosity was observed in the sintering temperature 800 ºC due to particle agglomeration.



(a) (b)

(c)

Figure 2 SEM microphotograph of $LaCo_{0.6}Fe_{0.4}O_3$ ceramics sintered at (a) 800 ºC (b) 900 ºC (c) 1000 ºC

FT IR analysis

FT IR spectra of $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline ceramics are presented in Figure 3 and Table 2. The respective metal-oxygen stretching vibrations are observed in FT IR spectra for all samples sintered at different temperatures (800 °C, 900 °C and 1000 °C). The FT IR spectrum of $LaCo_{0.6}Fe_{0.4}O_3$ has characteristics bands at 408 cm^{-1} and 666 cm^{-1} that ascribed to the vibration of metal oxygen bond. La-O absorption band appeared between 400 cm^{-1} and 450 cm^{-1}. The strong absorption band between 500 cm^{-1}-650 cm^{-1} are assigned to Co-O stretching vibration and that between 550 cm^{-1}-700 cm^{-1} are indicated Fe-O-Fe stretching vibration (Nakamoto *et al*., 1970).

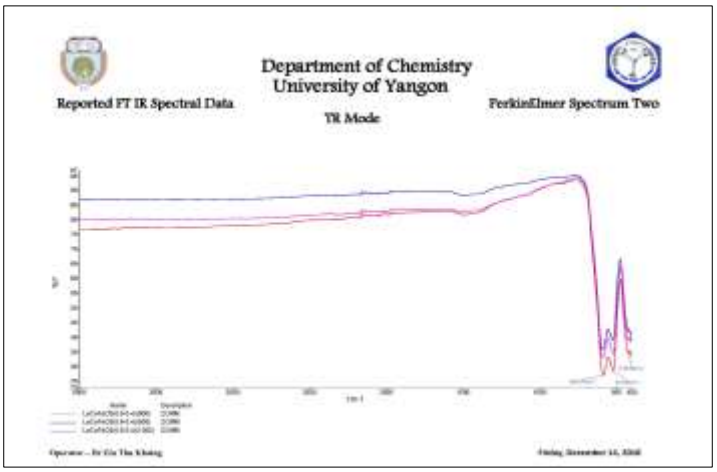


Figure 3 FT IR spectra of $LaCo_{0.6}Fe_{0.4}O_3$ ceramics sintered at (800 ºC, 900 ºC and 1000 ºC)

Table 2 FT IR Spectral Data of the $LaCo_{0.6}Fe_{0.4}O_3$ Ceramics by Citrate Sol-gel Method after Sintering at Different Temperatures

Observed Wavenumber (cm^{-1})	Literature Wavenumber* (cm^{-1})	Band Assignment
416	400-450	Stretching vibration of La-O group
519	500-650	Stretching vibration of Fe-O group
580	550-700	Stretching vibration of Co-O group

*Nakamoto (1970)

Electrical Properties

The electrical properties of the pellet samples of $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline ceramics prepared by sol-gel method was studied at different temperatures using LCR (inductance, capacitance and resistance) meter. The dielectric properties and electrical properties of $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline ceramics was carried out to determine in the frequency range of 1 MHz-2 MHz. It was observed that the dielectric constant and dielectric loss tangent were found to decrease with increase in frequencies. The dielectric constant was calculated by using the formula $\sigma = Cd/\varepsilon_0 A$ 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. Thus σ_{ac} depends strongly on the frequency of the applied field (Priyanka *et al*., 2013). At high temperature the dielectric constant and dielectric loss tangent (tan δ) increased significantly as the frequency decreased for the $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline ceramics as shown in Figures 4 and 5, and Tables 3 and 4. In the high temperature region, higher value of dielectric constant may be related to polarization which comes from mobility of ions and imperfections from this material. 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 *et al*., 2015). Figure 6 and Table 5 show the variation of ac conductivity of $LaCo_{0.6}Fe_{0.4}O_3$ ceramics sintered at different temperatures as a function of frequency. It was noted that σ_{ac} increased with increasing frequency for all the temperatures. AC conductivity indicates that the conduction occurs by the hopping of charge carrier between localized states. It was observed that the ac conductivity of $LaCo_{0.6}Fe_{0.4}O_3$

ceramics increased with an increase in temperatures related to the enormous hopping of charge carriers. The resistivity values of the samples were found to decrease with increase in frequency. The resistivity of $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline ceramics at 1000 °C was greater than those of other two temperatures as shown in Figure 7 and Table 6. The resistivity is inversely proportional to dc conductivity. The high value of resistivity has the lower value dc conductivity for all the temperatures as shown in Figure 8 and Table 7. The dc conductivity value of $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline ceramics increased when temperature was raised.

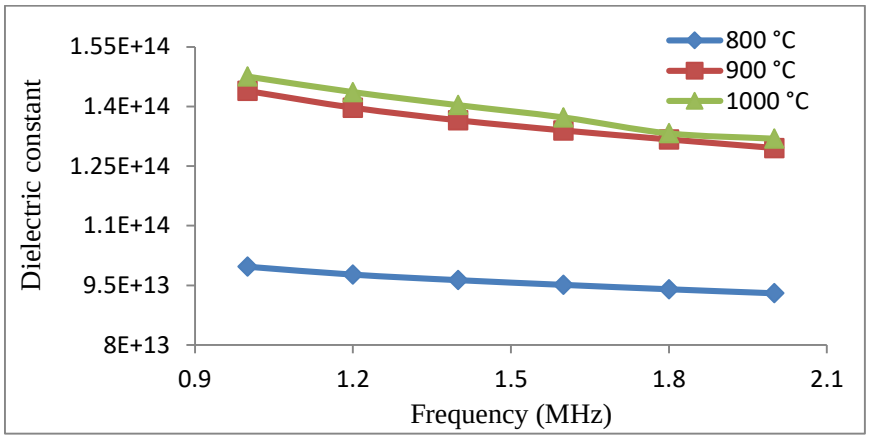


Figure 4 Variation of dielectric constant of $LaCo_{0.6}Fe_{0.4}O_3$ ceramics prepared by sol-gel method sintered at different temperatures as a function of frequency

Table 3 Variation of Dielectric Constant of $LaCo_{0.6}Fe_{0.4}O_3$ Ceramics Sintered at Different Temperatures as a Function of Frequency

Frequency (MHz)	Dielectric constant		
	800 °C	900 °C	1000 °C
1	9.97E+13	1.43E+14	1.48E+14
1.2	9.77E+13	1.39E+14	1.44E+14
1.4	9.63E+13	1.36E+14	1.40E+14
1.6	9.51E+13	1.33E+14	1.37E+14
1.8	9.40E+13	1.31E+14	1.33E+14
2	9.30E+13	1.29E+14	1.32E+14

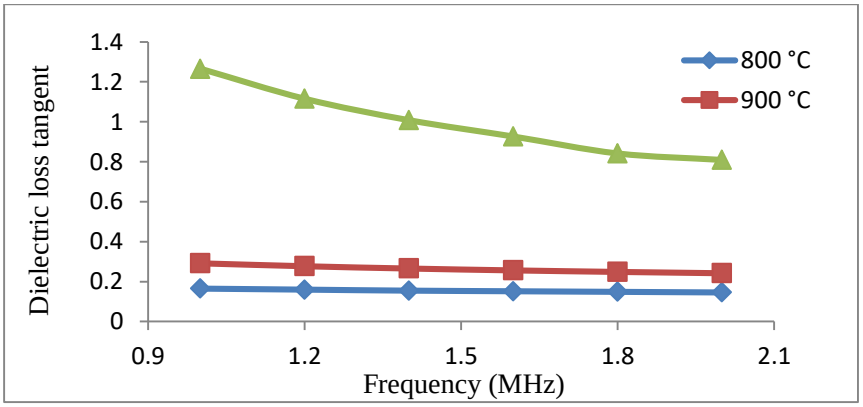


Figure 5 Variation of dielectric loss tangent of $LaCo_{0.6}Fe_{0.4}O_3$ ceramics sintered at different temperatures as a function of frequency

Table 4 Variation of Dielectric Loss tangent of $LaCo_{0.6}Fe_{0.4}O_3$ Ceramics Sintered at Different Temperatures as a Function of Frequency

Frequency (MHz)	Dielectric loss tangent		
	800 °C	900 °C	1000 °C
1	0.165	0.291	1.265
1.2	0.160	0.277	1.115
1.4	0.155	0.265	1.008
1.6	0.152	0.256	0.926
1.8	0.149	0.249	0.841
2	0.146	0.242	0.809

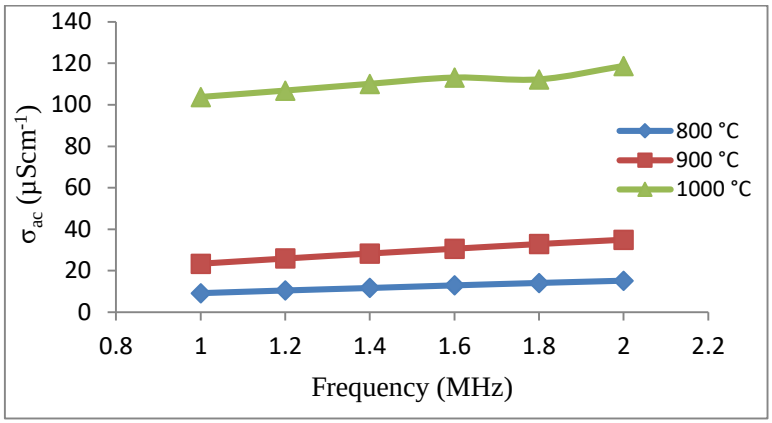


Figure 6 Variation of ac conductivity of $LaCo_{0.6}Fe_{0.4}O_3$ ceramic sintered at different temperatures as a function of frequency

Table 5 Variation of ac Conductivity of $LaCo_{0.6}Fe_{0.4}O_3$ Ceramic Sintered at Different Temperatures as a Function of Frequency

Frequency (MHz)	AC Conductivity (μScm^{-1})		
	800 °C	900 °C	1000 °C
1	9.140	23.329	103.734
1.2	10.424	25.825	106.817
1.4	11.614	28.231	110.082
1.6	12.857	30.549	113.097
1.8	14.015	32.799	112.241
2	15.095	34.882	118.711

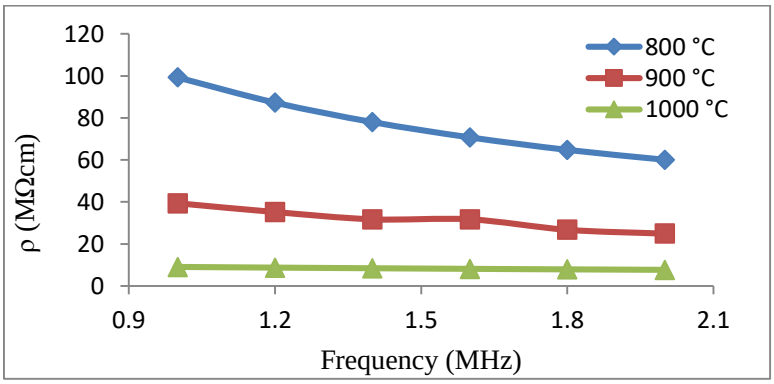


Figure 7 Variation of resistivity of $LaCo_{0.6}Fe_{0.4}O_3$ ceramics sintered at different temperatures as a function of frequency

Table 6 Variation of Resistivity of $LaCo_{0.6}Fe_{0.4}O_3$ Ceramics Sintered at Different Temperatures as a Function of Frequency

Frequency (MHz)	Resistivity (MΩcm)		
	800 °C	900 °C	1000 °C
1	99.28	39.30	8.98
1.2	87.30	35.16	8.67
1.4	78.01	31.73	8.38
1.6	70.73	31.71	8.11
1.8	64.77	26.78	7.87
2	60.08	24.96	7.66

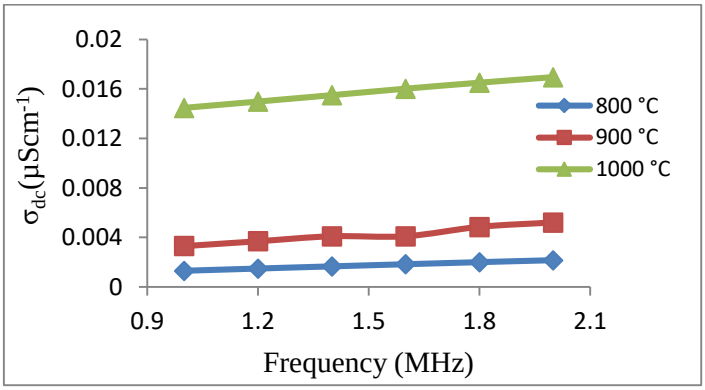


Figure 8 Variation of dc conductivity of $LaCo_{0.6}Fe_{0.4}O_3$ ceramics sintered at different temperatures as a function of frequency

Table 7 Variation of dc Conductivity of $LaCo_{0.6}Fe_{0.4}O_3$ Ceramics Sintered at Different Temperatures as a Function of Frequency

Frequency (MHz)	DC Conductivity (μScm^{-1})		
	800 °C	900 °C	1000 °C
1	0.0013	0.0033	0.0144
1.2	0.0014	0.0036	0.0149
1.4	0.0016	0.0041	0.0154
1.6	0.0018	0.0041	0.0160
1.8	0.0020	0.00481	0.0165
2	0.0021	0.00521	0.0169

Optical Properties

UV-visible absorption spectroscopic method is a powerful technique to explore the optical properties of semiconducting nanoparticles. The optical properties of the prepared $LaCo_{0.6}Fe_{0.4}O_3$ ceramics at different temperatures 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 gaps of $LaCo_{0.6}Fe_{0.4}O_3$ samples were calculated from the Tauc's plots of $(\alpha h\nu)^2$ vs $h\nu$. The optical band gap of the ceramic samples were 2.2 eV for 800 °C, 2.1 eV for 900 °C and 2.0 eV for 1000 °C (Figure 9 and Table 8). 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.

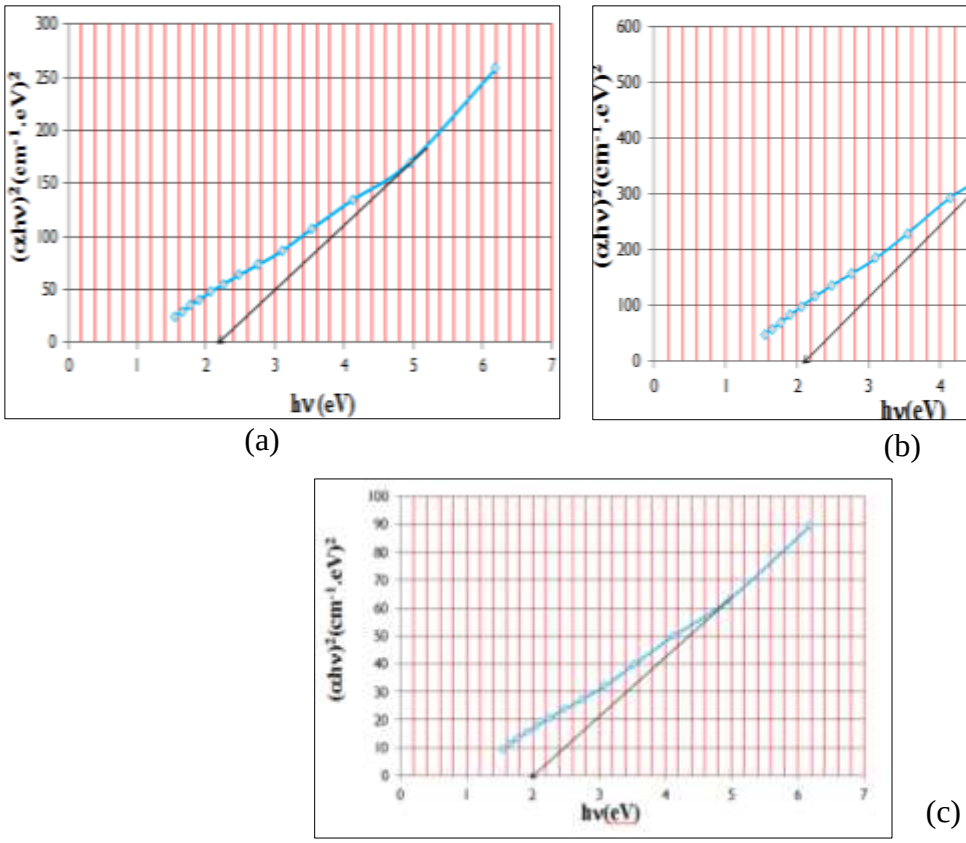


Figure 9 Plot of $(\alpha h\nu)^2$ against $h\nu$ for $LaCo_{0.6}Fe_{0.4}O_3$ ceramics sintered at (a) 800 ºC (b) 900 ºC and (c) 1000 ºC

Table 8 Band Gap Values of $LaCo_{0.6}Fe_{0.4}O_3$ Ceramics Sintered at Different Temperatures

$LaCo_{0.6}Fe_{0.4}O_3$	Band gap values (eV)
800	2.2
900	2.1
1000	2.0

Conclusion

$LaCo_{0.6}Fe_{0.4}O_3$ ceramics were sintered at different temperatures (800 °C, 900 °C and 1000 °C) for 1 h by citrate sol-gel method. The calculated sizes of $LaCo_{0.6}Fe_{0.4}O_3$ ceramics sintered at 800 °C, 900 °C and 1000 °C from Scherrer formula were found to be 25.7 nm, 27.6 nm and 32.6 nm, respectively. In the XRD pattern of the prepared sample after sintering at 1000 ºC, the peaks were sharper than those at 800 ºC and 900 ºC. FT IR spectra showed the presence of the stretching vibrations of metal-oxygen (La-O, Co-O and Fe-O) chemical bonds. From SEM analysis, compact and dense nature was observed. The optical band gap of $LaCo_{0.6}Fe_{0.4}O_3$ ceramic samples were found to be 2.2 eV for $LaCo_{0.6}Fe_{0.4}O_3$ sample at 800 °C, 2.1 eV for 900 °C and 2.0 eV for 1000 °C. The ac conductivity and dielectric properties of $LaCo_{0.6}Fe_{0.4}O_3$ ceramic samples were studied at the frequency range of 1 MHz-2 MHz. The frequency depends of ac conductivity. Both dielectric constant and dielectric loss tangent were found to decrease with increase in frequency and increase with increase in temperature.

Acknowledgments

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