STUDY ON THE STRUCTURAL, ELECTRICAL AND OPTICAL PROPERTIES OF $LiNi_{1-x}Co_xO_2$ ($0.3 \leq x \leq 0.5$) NANOCRYSTALLINE POWDER BY SOL–GEL METHOD

Naw Mon Thae Oo[1], Hnin Yu Wai[2], KhinThan Yee[3]

Abstract

The main aim of the research is to study structural, electrical and optical properties of $LiNi_{1-x}Co_xO_2$ ($0.3 \leq x \leq 0.5$) nanocrystalline powder. $LiNi_{1-x}Co_xO_2$ ($0.3 \leq x \leq 0.5$) nanocrystalline powders were prepared by a modified sol–gel method using lithium nitrate ($LiNO_3$), cobalt(II) nitrate ($Co(NO_3)_2.6H_2O$) and nickel(II) nitrate ($Ni(NO_3)_2.6H_2O$) as starting materials, de-ionized water as solvent, citric acid ($C_6H_8O_7.H_2O$) as chelating agents and carboxy methyl cellulose as dispersant agent. The prepared samples were calcined at 800 °C. The calcined powder was made as pellet form by using cold pressing method. The pellets were sintered at 900 °C. The pellets of $LiNi_{1-x}Co_xO_2$ were characterized by XRD, FT IR and SEM. Electrical properties were examined by LCR meter in the frequency range 100 kHz – 2 MHz and frequency depended on prepared sample. The optical properties were investigated by UV-Vis spectrophotometer. From XRD data, the observed values of the average crystallite sizes of $LiNi_{0.7}Co_{0.3}O_2$, $LiNi_{0.6}Co_{0.4}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$ sintered at 900 °C were 13.58 nm, 44.31 nm and 48.03 nm, respectively. By increasing Co doping level, the average crystallite size also increased. FT IR spectra indicated the presence of the stretching vibrations of metal-oxygen (Ni-O and Co-O) chemical bonds. The spherical-shaped nanocrystalline powders were observed in SEM images. Electrical measurement revealed that the ac conductivity increased with increase in frequency. The ac conductivity of $LiNi_{0.5}Co_{0.5}O_2$ was lower than those of other two prepared nanopowder samples ($LiNi_{0.7}Co_{0.3}O_2$ and $LiNi_{0.6}Co_{0.4}O_2$). The value of ac conductivity was between 10^{-2} and 10^{-4} S cm^{-1}. Dielectric constants and dielectric loss were found to decrease with increase in frequency. The experimental results indicated that the ac conductivity, dielectric constant and dielectric loss of prepared samples depend on the frequencies. From UV-Vis data, the optical band gap values of $LiNi_{0.7}Co_{0.3}O_2$, $LiNi_{0.6}Co_{0.4}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$ nanopowder samples were found to be 3.2, 3.4 and 3.6 eV, respectively. These band gap values (E_g) are also reliable within semiconductor band gap range.

Keywords: $LiNi_{1-x}Co_xO_2$ crystalline nanopowders, cold pressing method, ac conductivity, optical band gap

Introduction

$LiNi_{0.8}Co_{0.2}O_2$, a nickel-rich phase $LiNi_{1-x}Co_xO_2$ system, crystallizes in R $\bar{3}$ m space group with hexagonal ordering isostructural to $LiCoO_2$ and $LiNiO_2$. Small amount of cobalt in the frame work of $LiNi_{1-x}Co_xO_2$ reduce Jahn-Teller distortion of Ni^{3+} ions and help minimizing structural strain associated with distorted NiO_6 octahedra (Sathiya *et al*., 2011). $LiNi_{1-x}Co_xO_2$ (LNCO) are of great interest for use as positive electrode in rechargeable lithium-ion batteries because of their high specific capacity high voltage and long cycle-life (Baskaran *et al*., 2009). Oxide nanomaterials have been drawing wide attention due to their comparatively excellent electrical, optical or magnetic properties. Their properties such as electrical, optical, etc. can be tuned by engineering size, morphology or composition (Indulal *et al.*, 2017). The aim of this study was to prepare $LiNi_{1-x}Co_xO_2$ ($0.3 \leq x \leq 0.5$) nanocrystalline powders by a modified sol–gel method and to investigate the ac conductivity and dielectric properties of the prepared $LiNi_{1-x}Co_xO_2$, nanopowders.

[1] PhD Candidate, Department of Chemistry, University of Yangon
[2] Dr, Lecturer, Department of Chemistry, University of Yangon
[3] Dr, Lecturer, Department of Chemistry, University of West Yangon

Materials and Methods

Sample Collection

Lithium nitrate, cobalt nitrate, nickel nitrate, citric acid, carboxy methyl cellulose were purchased from BDH Chemicals Ltd., Poole, England. Citric acid was used as a chelating agent and carboxy methyl cellulose as a dispersant agent. Distilled water was used as the solvent in all analyses.

Preparation of $LiNi_{1-x}Co_xO_2$ ($0.3 \leq x \leq 0.5$) Nanocrystalline Powder

$LiNi_{0.7}Co_{0.3}O_2$, $LiNi_{0.6}Co_{0.4}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$ nanocrystalline powders were prepared by sol-gel method using lithium nitrate, cobalt nitrate, nickel nitrate, citric acid and carboxy methyl cellulose (Zhu *et al*., 2010). Firstly, 6.9 g each of lithium nitrate, 20.35 g, 17.44 g and 14.54 g of nickel (II) nitrate and 8.73 g, 11.64 g and 14.55 g of cobalt (II) nitrate salts were added into 100 mL each of deionized water in three separate beakers to obtain molar ratios of 1:0.7:0.3, 1:0.6:0.4 and 1:0.5:0.5, respectively. Next, 42 g of citric acid (the molar ratio of citric acid/ total metal ions = 1) was added into 100 mL of deionized water. The individual solutions were mixed and after that with a small amount of carboxy methyl cellulose (the molar ratio of cellulose to total cations was 5×10^{-6}) was added into this solution. Each mixture solution was heated at 65 °C for 12 h under constant stirring to form the sol. The sol was then evaporated at 120°C in drying oven until the gel was formed. The gel solution was calcined at 800 °C for 4 h. Finally, the samples were finely ground in an agate mortar.

Preparation and Characterization of Pellets

The calcined black powders $LiNi_{1-x}Co_xO_2$ were pressed into pellets with diameter 1.256 cm and thickness 0.3 cm using MAEKAWA Testing machine. The pellets were sintered at temperature 900^0C for 4 h. The resulting pellet was characterized by XRD, SEM, FT IR techniques. The electrical and optical properties were investigated by LCR meter and UV-Vis spectrophotometer, respectively.

X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray Diffractometer, RINI 2000/PC software, Cat. No 9240 J 101, Japan. FT IR spectrum was recorded in the range of 4000-400 cm^{-1} by using Perkin Elmer spectrum Two, FT IR spectrophotometer. The scanning electron microscopy (SEM) images were obtained using JSM-5610 Model SEM, JEOL-Ltd., Japan.

For the electrical conductivity measurements, the obtained samples were pressed in the form of pellet using MAEKAWA Testing machine. The dielectric permittivities such as D, K and tangent loss of composites were determined using LCR-B110G meter (DC 20-10 Hz) in the frequency range of 100 kHz-2 MHz at ambient temperature. Frequency dependent electrical conductivity was evaluated by using dielectric equation (Tharayil *et al*., 2008).

$$C = \frac{K \varepsilon_0 A}{d},\ \tan\delta = D = 1/(2\pi f R_p C_p),\ \omega = 2\pi f',\ \sigma_{ac} = \omega \tan\delta\ K\ \varepsilon_o$$

where, C is capacitance (pF), K is dielectric constant, ε_0 is electrical permittivity in vacuum (8.85×10^{-14} F cm^{-1}), d is sample thickness (cm), ω is circular frequency (MHz), D is dielectric loss factor (D), tan δ is dielectric loss tangent and σ_{ac} is electrical conductivity (S cm^{-1})**.**

Measurement of Optical Properties

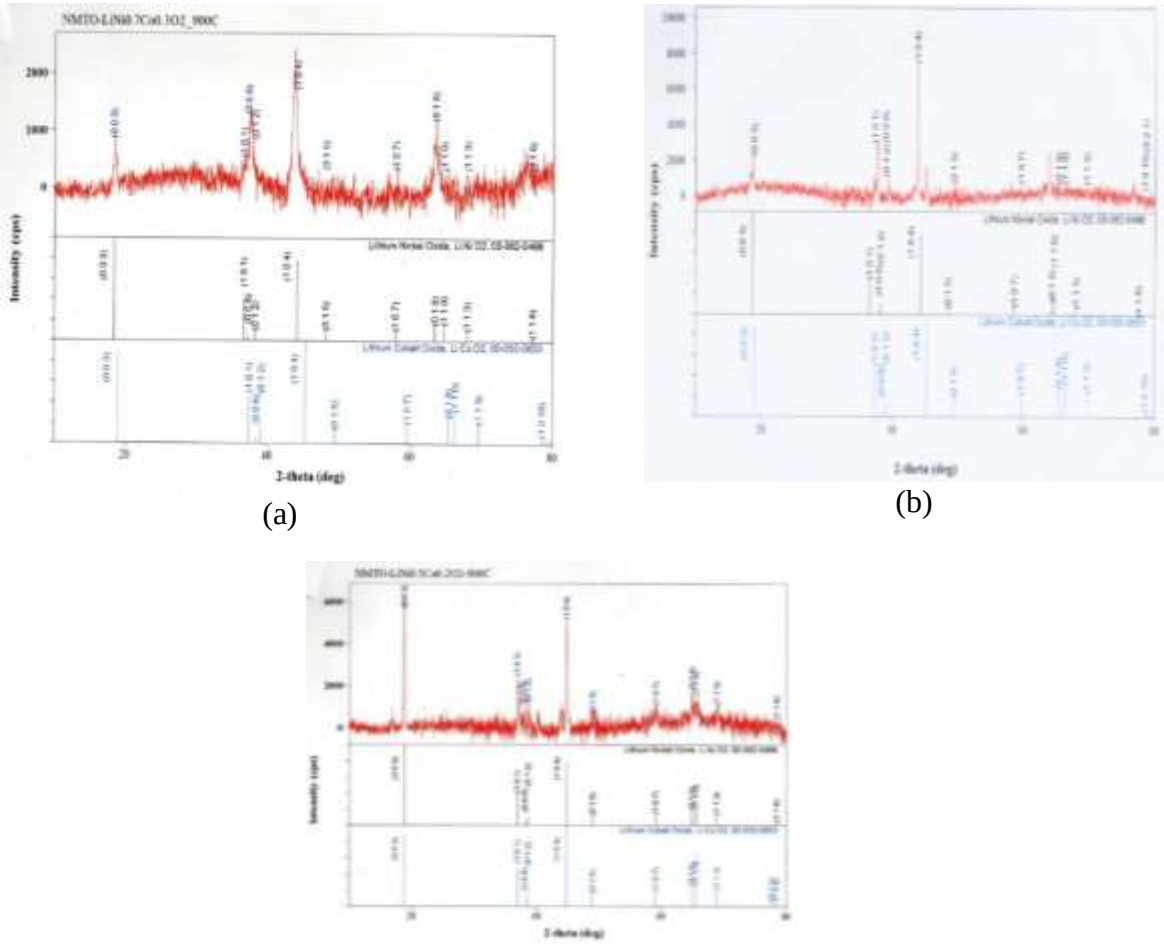
Energy band gap of materials is related to absorption coefficient α by the Tauc's relationship. $\alpha h\nu = A\ (h\nu - E_g)^n$ where α is absorption coefficient (α = 2.303 A/t, where A is the

absorbance and t is the denoted thickness of the cuvette), A is constant, hν is photon energy and E_g is band gap (Tharayil *et al*., 2008).

Results and Discussion

XRD Analysis

The XRD patterns of the prepared $LiNi_{0.8}Co_{0.2}O_2$ nanocrystalline powders sintered at 900 °C are shown in Figure 1 and the average crystallite size, crystal system and lattice parameter are listed in Table 1. By increasing Co doping level, it was found that the diffraction peaks of pellet were narrow and more clear sharp peak at this temperature. The crystallite size of $LiNi_{1-x}Co_xO_2$ nanocrystalline powder was calculated by using Scherrer's equation (Ahmed *et al*., 2012).



(a) (b)

(c)

Figure 1 X-ray diffraction patterns of (a) $LiNi_{0.7}Co_{0.3}O_2$ (b) $LiNi_{0.6}Co_{0.4}O$ and (c) $LiNi_{0.5}Co_{0.5}O_2$ powders sintered at 900 °C for 4 h

Table 1 Average Crystallite Size of the Prepared $LiNi_{1-x}Co_xO_2$ Powders

Samples	Average crystallite size (nm)	Lattice parameters (Å)		Crystal system
		a	c	
$LiNi_{0.7}Co_{0.3}O_2$	13.58	2.7979	14.1885	Hexagonal
$LiNi_{0.6}Co_{0.4}O_2$	44.31	2.8412	14.0712	Hexagonal
$LiNi_{0.5}Co_{0.5}O_2$	48.03	2.8386	13.9974	Hexagonal

FT IR Analysis

FT IR data indicated the presence of functional groups in the $LiNi_{1-x}Co_xO_2$ powder. The FT IR spectra of the prepared $LiNi_{1-x}Co_xO_2$ powder sintered at 900 °C are shown in Figure 2 and the spectral assignments shown in Table 2. In the spectrum of $LiNi_{1-x}Co_xO_2$ nanocrystalline powder, the peaks indicated the stretching vibration of metal oxygen bond (Nakamoto, 1970).

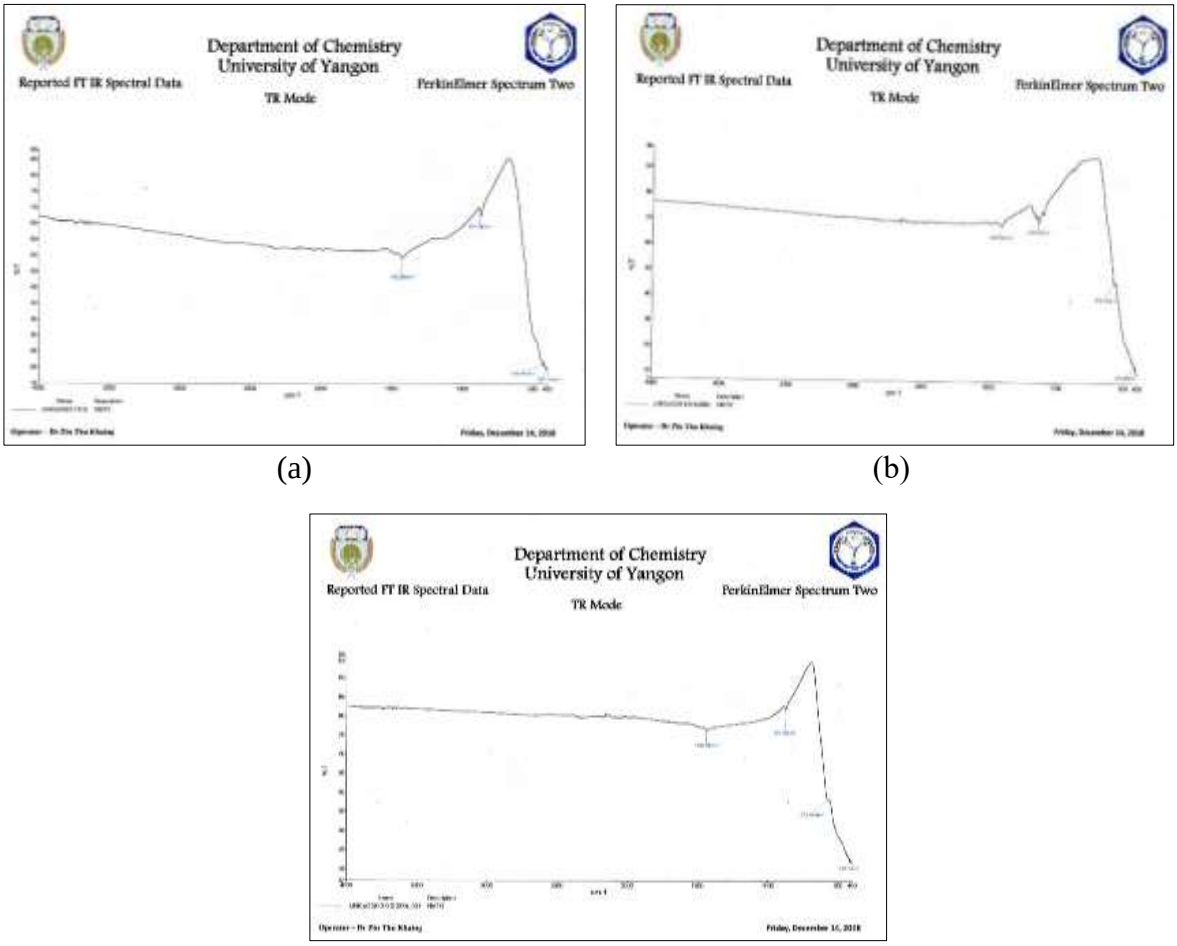


Figure 2 FT IR spectra of (a) $LiNi_{0.7}Co_{0.3}O_2$ (b) $LiNi_{0.6}Co_{0.4}O$ and (c) $LiNi_{0.5}Co_{0.5}O_2$ powders sintered at 900 °C for 4 h

Table 2 Band Assignments of FT IR Spectra of the Prepared $LiNi_{1-x}Co_xO_2$ Powders Sintered at 900 °C for 4 h

Observed wavenumber (cm^{-1})			*Literature wavenumber (cm^{-1})	Band assignments
$LiNi_{0.7}Co_{0.3}O_2$	$LiNi_{0.6}Co_{0.4}O_2$	$LiNi_{0.5}Co_{0.3}O_2$		
-	573	572	650-400	Stretching vibration of Co/Ni-O bond
427 407	416	412		

*Nakamoto, 1970

SEM Analysis

Surface morphology was studied by obtaining micrographs using JOEL-JSM-5610, Japan, Ion sputter-JEC-1600 (Sahoo *et al.*, 2010). The morphology of prepared $LiNi_{1-x}Co_xO_2$ powder was investigated by SEM. The SEM images of all the samples of $LiNi_{1-x}Co_xO_2$ sintered at 900 ºC showed the spherical agglomeration of porous nature and irregular shaped morphology (Figure 3).

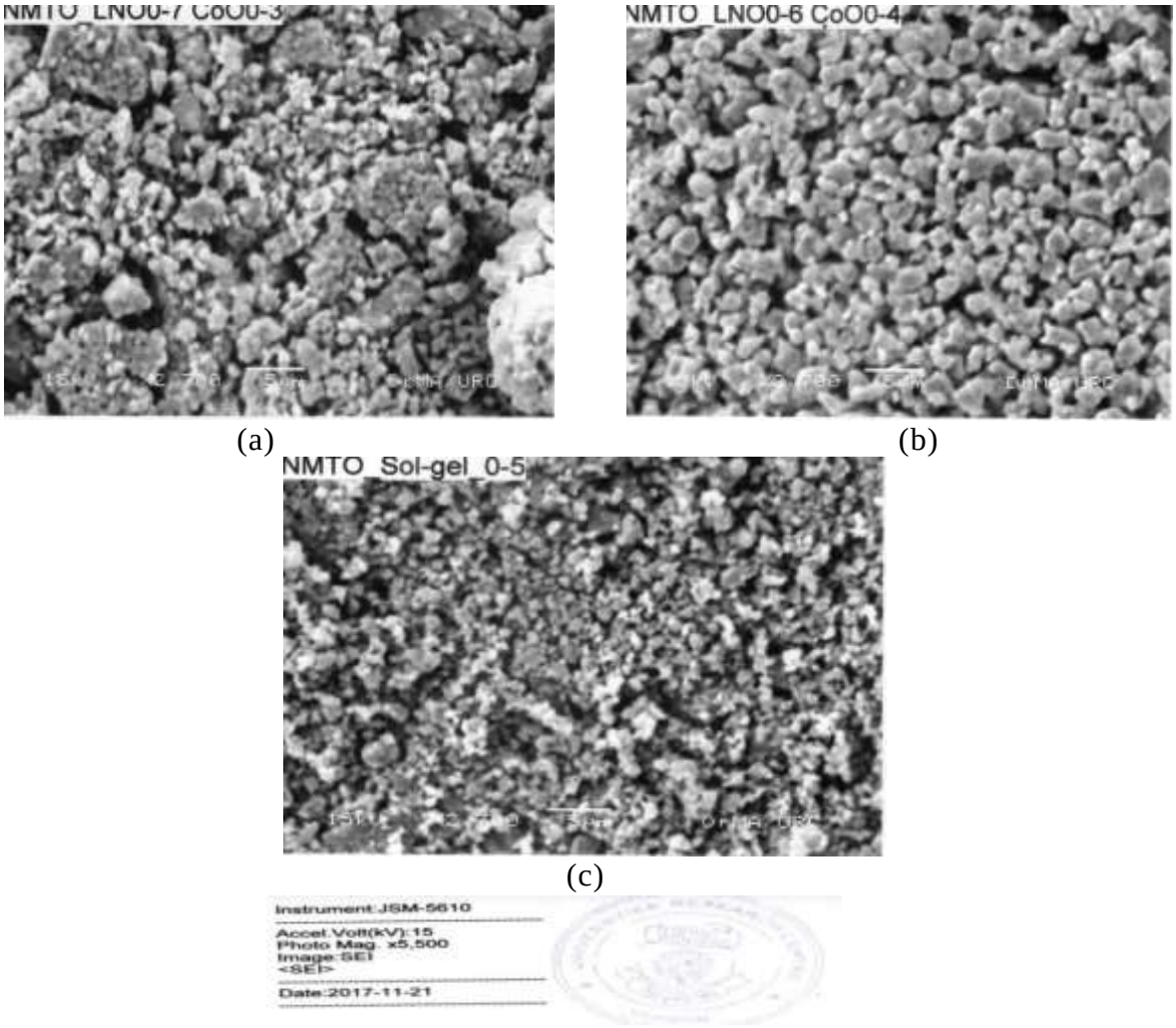


Figure 3 SEM micrographs of (a) $LiNi_{0.7}Co_{0.3}O_2$ (b) $LiNi_{0.6}Co_{0.4}O$ and (c) $LiNi_{0.5}Co_{0.5}O_2$ powders sintered at 900 °C for 4 h

Electrical Properties

Electrical properties were examined by LCR meter in the frequency range 100 kHz –2 MHz. The ac conductivity of $LiNi_{0.5}Co_{0.5}O_2$ was lower than the other prepared samples ($LiNi_{0.7}Co_{0.3}O_2$ and $LiNi_{0.6}Co_{0.4}O_2$) nanopowders as shown in Table 3 and Figure 4. The value of ac conductivity was between 10^{-2} and 10^{-4} S cm^{-1}. The ac conductivity increased with increase in frequency. The dielectric constant decreased with increasing frequency (Table 4 and Figure 5). At higher frequency, dielectric loss Tan δ was also found to decrease as shown in Table 5 and Figure 6.

Table 3 Changes of AC Conductivity of Prepared $LiNi_{1-x}Co_xO_2$ as a Function of Frequency at 2V

Frequency (Hz)	Electrical conductivity (S cm^{-1})		
	$LiNi_{0.7}Co_{0.3}O_2$	$LiNi_{0.6}Co_{0.4}O_2$	$LiNi_{0.5}Co_{0.5}O_2$
100000	1.45E-02	1.06E-02	4.60E-04
400000	1.68E-02	1.22E-02	9.01E-04
800000	2.04E-02	1.48E-02	1.56E-03
1200000	2.35E-02	1.70E-02	2.13E-03
1600000	2.58E-02	1.87E-02	2.61E-03
2000000	2.76E-02	2.01E-02	3.03E-03

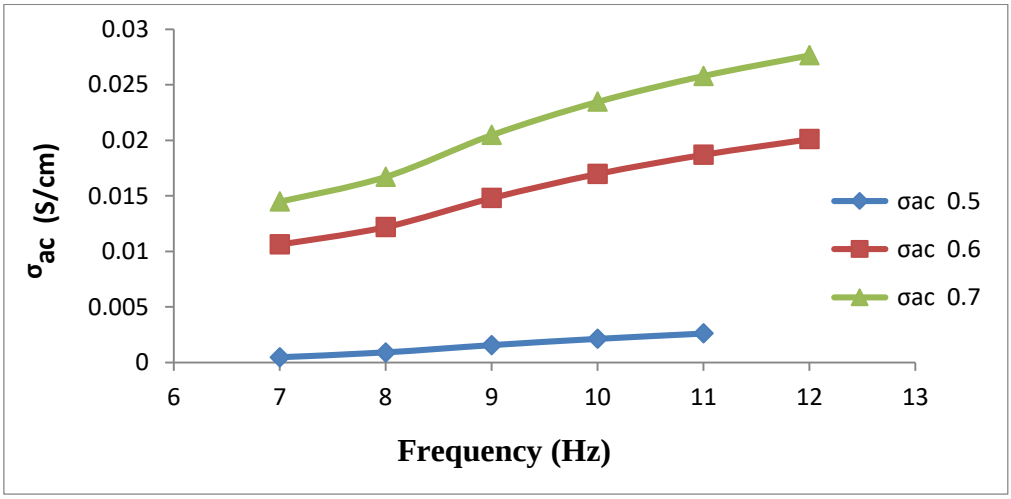


Figure 4 Variation of ac conductivity of prepared $LiNi_{1-x}Co_xO_2$ sintered at 900 °C as a function of frequency at 2 V

Table 4 Dielectric Constant (Tan δ) of Prepared $LiNi_{1-x}Co_xO_2$ as a Function of Frequency at 2V

Frequency (Hz)	Dielectric constant (K)		
	$LiNi_{0.7}Co_{0.3}O_2$	$LiNi_{0.6}Co_{0.4}O_2$	$LiNi_{0.5}Co_{0.5}O_2$
100000	5.42E+13	5.82E+13	1.55E+13
400000	4.77E+13	4.85E+13	1.28E+13
800000	4.27E+13	4.09E+13	1.14E+13
1200000	3.91E+13	3.59E+13	1.06E+13
1600000	3.68E+13	3.26E+13	1.01E+13
2000000	3.52E+13	3.03E+13	9.58E+12

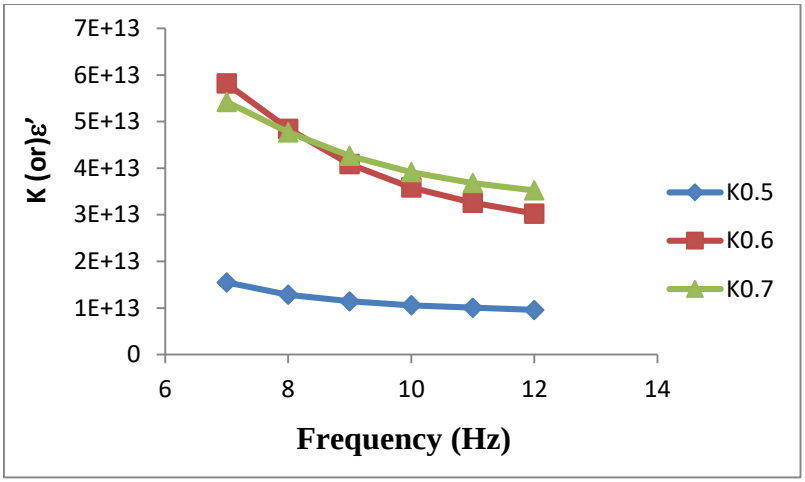


Figure 5 Variation dielectric constant of prepared $LiNi_{1-x}Co_xO_2$ sintered at 900 °C as a function of frequency at 2 V

Table 5 Dielectric Loss (Tan δ) of Prepared $LiNi_{1-x}Co_xO_2$ as a Function of Frequency at 2V

Frequency (Hz)	Dielectric loss (Tanδ)		
	$LiNi_{0.7}Co_{0.3}O_2$	$LiNi_{0.6}Co_{0.4}O_2$	$LiNi_{0.5}Co_{0.5}O_2$
100000	4.48E-09	3.52443E-09	5.35E-10
400000	1.55E-09	1.1492E-09	3.16E-10
800000	1.13E-09	7.7999E-10	3.07E-10
1200000	9.81E-10	6.50425E-10	3.01E-10
1600000	8.9E-10	5.71367E-10	2.92E-10
2000000	8.22E-10	5.13551E-10	2.85E-10

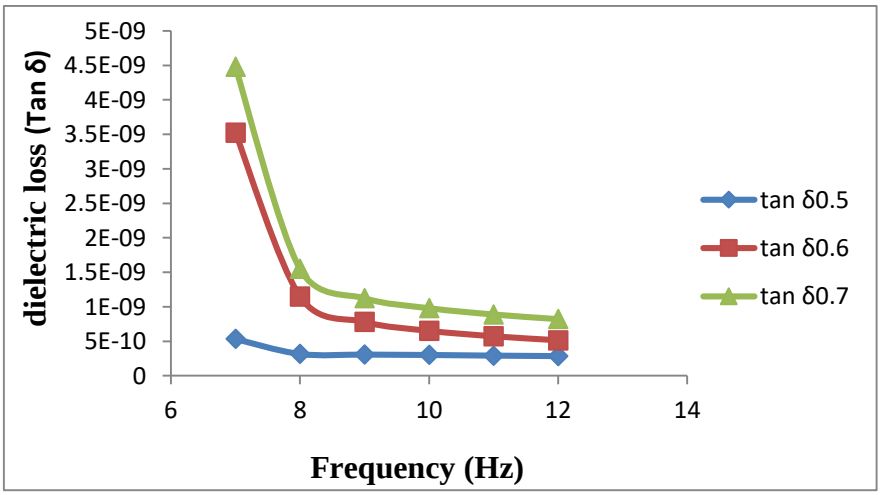
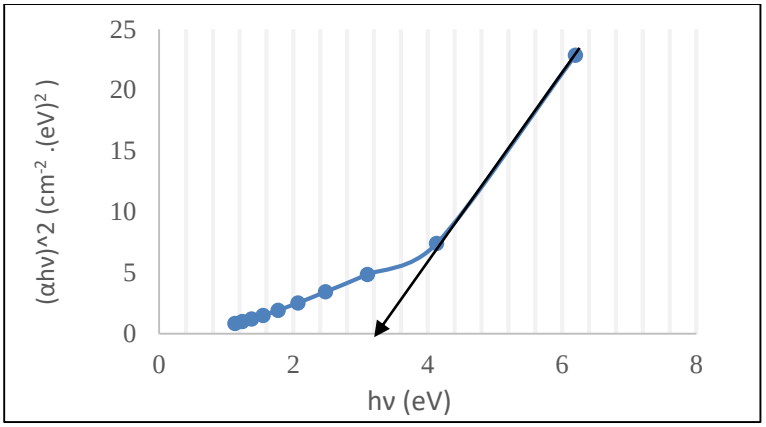


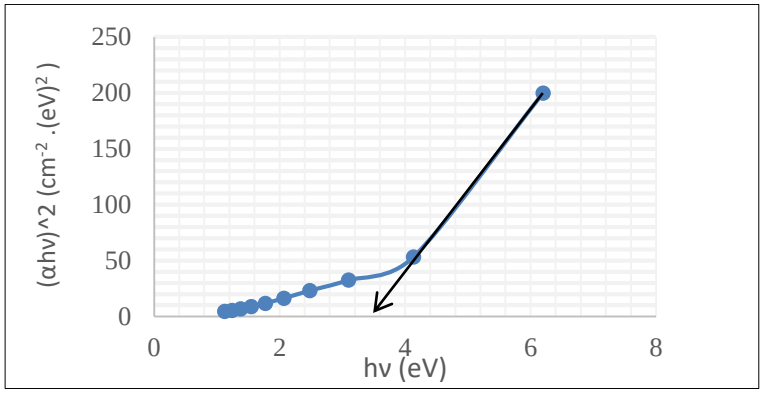
Figure 6 Variation dielectric loss of prepared $LiNi_{1-x}Co_xO_2$ sintered at 900 °C as a function of frequency at 2 V

Optical Properties

Figure 7 shows energy band gap for $LiNi_{0.7}Co_{0.3}O_2$, $LiNi_{0.6}Co_{0.4}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$ nanocrystalline powders. The optical band gap is obtained by Tauc's equation. The band gap values for $LiNi_{0.7}Co_{0.3}O_2$, $LiNi_{0.6}Co_{0.4}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$ powders were found to be 3.2, 3.4 and 3.6 eV, respectively.



(a)



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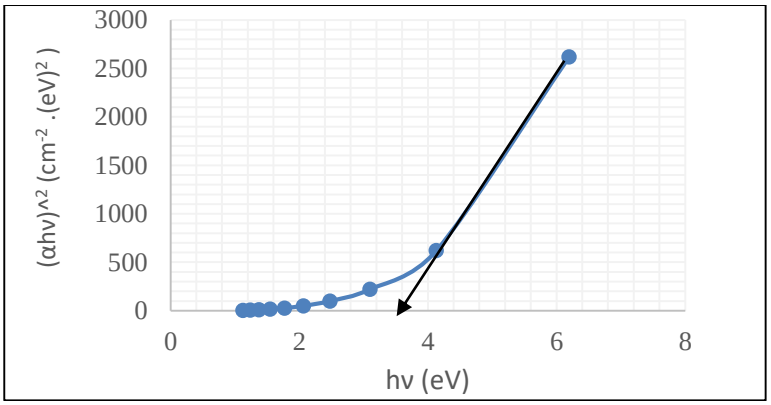

(c)

Figure 7 Tau's plot of (a)$LiNi_{0.7}Co_{0.3}O_2$ (b) $LiNi_{0.6}Co_{0.4}O_2$ and (c)$LiNi_{0.5}Co_{0.5}O_2$ at sintered temperature of 900 °C

Table 6 Optical Band Gap of the $LiNi_{1-x}Co_xO_2$ at Sintered Temperature (900 ˚C)

	Band gap (E_g) (eV)
$LiNi_{0.7}Co_{0.3}O_2$	3.2
$LiNi_{0.6}Co_{0.4}O_2$	3.4
$LiNi_{0.5}Co_{0.5}O_2$	3.6

Conclusion

$LiNi_{1-x}Co_xO_2$ nanocrystalline powder was prepared by using sol-gel method at sintering temperature of 900 °C. The crystallite sizes of $LiNi_{0.7}Co_{0.3}O_2$, $LiNi_{0.6}Co_{0.4}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$ nanocrystalline powders were calculated to be 13.58, 44.31 and 48.03 nm, respectively. By increasing Co doping level, the average crystallite size also increased. $LiNi_{1-x}Co_xO_2$ nanocrystalline powder was indexed as the hexagonal crystal system. FT IR analysis showed the presence of the stretching vibrations of metal-oxygen bonds in $LiNi_{1-x}Co_xO_2$ powders. SEM micrographs exhibited the spherical shape of prepared $LiNi_{1-x}Co_xO_2$ samples sintered at 900 °C. The optical band gap value (E_g) of the Co doped $LiNiO_2$ was calculated from the UV-Vis spectrum by using Tauc's plot relation. By increasing Co doping level, the optical band gap value was slightly increased. The ac conductivity of $LiNi_{0.5}Co_{0.5}O_2$ was lower than those of other prepared samples ($LiNi_{0.7}Co_{0.3}O_2$ and $LiNi_{0.6}Co_{0.4}O_2$) nanopowder. The dielectric studies showed that with decreasing frequency, dielectric constant and dielectric loss were found to increase.

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