STRUCTURAL CHARACTERISTIC, OPTICAL PROPERTIES AND AC ELECTRICAL CONDUCTIVITIES OF PEROVSKITE LaCoO$_3$ PREPARED BY DIFFERENT METHODS

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Abstract

Perovskite LaCoO$_3$ material was prepared by two different methods; citrate sol-gel and co-precipitation methods. The simple low temperature synthesis has been presented of single phased LaCoO$_3$ for cathode application in solid oxide fuel cell (SOFC). The X-ray diffraction (XRD) shows that the hexagonal LaCoO$_3$ phase was well formed at sintering temperature 900 °C in the citrate sol-gel and co-precipitation methods. Scanning electron microscopy (SEM) analysis indicates that the particle size of LaCoO$_3$ powder varies from 20 nm to 60 nm depending on the preparation method. The FT IR spectra confirm that the absorption band of La-O and Co-O bonding appeared at 665, 592 and 406 cm^{-1}. The optical properties of LaCoO$_3$ studied by UV-visible spectrophotometer in the wavelength range of 300 nm to 700 nm. The band gap values of the LaCoO$_3$ prepared by citrate sol-gel method and by co-precipitation are 2.15 eV and 2.42 eV respectively. The dielectric properties and ac electrical conductivity have been investigated by LCR meter in the frequency range of 100- 1000 kHz. The ac electrical conductivity value of LaCoO$_3$ prepared by citrate sol-gel method is 8.74 μΩcm^{-1} and by co-precipitation method is 4.38 μΩcm^{-1} respectively. The perovskite LaCoO$_3$ prepared by citrate sol-gel method show highly dense structure, lower band gap value and high electrical conductivity than the LaCoO$_3$ obtained by co-precipitation method.

Keywords: Perovskite, LaCoO$_3$, citrate sol-gel method, co-precipitation, optical band gap, ac electrical conductivity

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. Many superconducting ceramic materials (the high temperature superconductors) have perovskite-like structures, often with 3 or more metals including copper, and some oxygen positions left vacant. One prime example is yttrium barium copper oxide which can be insulating or superconducting depending on the oxygen content. Important properties of perovskite for their catalytic applications include the stability of mixed and unusual valence states of the transition metal ions in their structure, the presence of defect sites, and the high mobility of oxygen ions. When compared to noble metal-based catalysts, perovskite have better thermal stability, are less sensitive towards poisoning by sulfur, phosphorus and halogens, and are less expensive (Kenta and Kumar, 2014). The La-based perovskite of LaCoO$_3$ was very interesting compounds and their application can be found in many fields The LaCoO$_3$ find application in the field of catalyst, 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$_3$ nanocrystalline samples were synthesized by citrate sol-gel method

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and co-precipitation method and their structural, optical and ac electrical conductivities were investigated for further applications.

Materials and Methods

Synthesis of Perovskite LaCoO₃ Powders

Perovskite $LaCoO_3$ 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 $(NO_3)_3$.$6H_2O$ and Co $(NO_3)_2.6H_2O$ were used as starting materials for preparation of $LaCoO_3$. Lanthanum nitrate (7.52 g) and Cobalt nitrate (11.6 g) were dissolved in deionized water by stirring at room temperature. The citric acid solution used as chelating agent was added to the above solution. Molar ratio between the citric acid and metal nitrate was 2:1. Then ethylene glycol (5 mL) used as gelification agent was also added to the mixture solution. The purple coloured solution was heated at 80 °C under continuous stirring. After being heated for about 6 h, the solution becomes highly viscous and the purple transparent gel was formed. The gel was dried completely at an oven at 120 °C for 4 h. The dried gels were grounded with mortar and pestle. Finally, $LaCoO_3$ particles were obtained (Khetre *et al*., 2010). The xerogel dried powder was calcined at 450 °C 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 900 °C for 4 h. The citrate sol-gel synthesis occurs according to the following overall reaction (1) which gives rise to perovskite powders and gaseous species.

$$\text{La }(NO_3)_3.6H_2O + \text{Co }(NO_3)_2.6H_2O + nC_6H_8 O_7 + nC_2H_6O_2 \xrightarrow{\Delta} LaCoO_3 + nCO_2\uparrow + nN_2\uparrow + nH_2O \qquad (1)$$
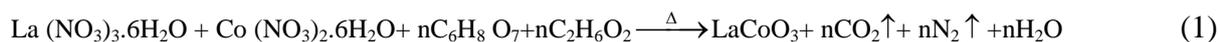
The second method, $LaCoO_3$ was prepared by co-precipitation in which nitrate precursors La $(NO_3)_3$.$6H_2O$ and Co $(NO_3)_2.9H_2O$ were mixed in the required stoichiometric ratio (i.e. La/Co = 1/1) to make aqueous solution. Lanthanum nitrate (7.52 g) and Cobalt nitrate (5.58 g) were dissolved in deionized water by stirring at room temperature. Ammonium carbonate (5.77 g) was dissolved in deionized water. And then ammonium carbonate solution was added to the above mixture solution. Both solutions were mixed together under continuous stirring for 30 min to ensure completion of reaction and pH was maintained at 7. Then the precursor powders precipitated were filtered and dried in oven at 110 °C. The dried precipitates were grounded to getas-prepared powder andthe calcined at 500 °C for 4 h. Finally $LaCoO_3$ powders were obtained. 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 900 °C for 4 h (Anupama and Prasad, 2015). The precipitation and calcination reactions may be represented by equations (2), (3) and (4), respectively.

$$\text{La }(NO_3)_3 .6H_2O + (NH_4)_2 CO_3 + nH_2O \longrightarrow La^{3+} + nCO_3^{2-} + nNH_4^+ + nNO_3^- \qquad (2)$$

$$\text{Co }(NO_3)_2.6H_2O + (NH_4)_2 CO_3 + nH_2O \longrightarrow Co^{3+} + nCO_3^{2-} + nNH_4^+ + nNO_3^- \qquad (3)$$

$$La^{3+} + Co^{3+} + nCO_3^{2-} + nNH_4^+ + nNO_3^- \longrightarrow LaCoO_3 + n CO_2\uparrow + nN_2\uparrow + nH_2O \qquad (4)$$
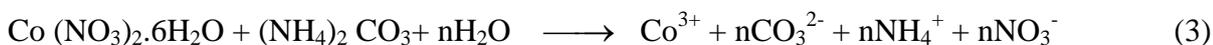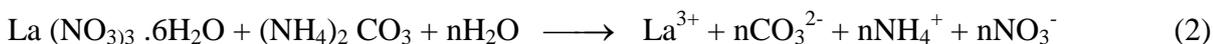
Characterization of the Prepared Perovskite LaCoO₃

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$_\alpha$ radiation (λ=1.5405Å). 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 λ/β cos θ, where λ is X-ray wavelength and β is peak width at half maximum. The FT IR measurements have been performed in the region of 400-4000 cm^{-1} by using 8400 SHIMADZU, Japan FT IR spectrometer. 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 Discussion

The perovskite LaCoO₃ was prepared by citrate sol-gel and co-precipitation method. The precursor powders of perovskite prepared by two methods were calcined at different temperature 450 °C 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 of perovskite LaCoO₃ powders obtained by the two different methods were sintered at 900 °C for 4 h. The perovskite samples obtained from two methods were characterized by TG-DTA, XRD, FT IR and SEM analysis. The crystalline pellets were characterized by XRD, FT IR and SEM analysis. The optimum sintering temperature was 900 °C and the average crystallite size was found 40.93 nm. At 900 °C, the XRD patterns of the two methods showed that the major phase of LaCoO₃ with hexagonal crystalline structure. The optical properties of perovskite LaCoO₃ obtained from two methods were studied by UV-visible absorption spectroscopy. Frequency dependence dielectric behavior of the pellet samples were determined by LCR meter.

Thermal Analysis

Thermal analysis can be utilized to identify the thermal stability and the decomposition temperature of the prepared perovskite. Figure 1 shows TG-DTA thermogram of dried LaCoO₃ xerogel powder prepared by citrate sol-gel. It was observed that two exothermic peaks at 170 °C and 412 °C formed in DTA thermogram. The two exothermic peaks related to the combustion and decomposition of organic residues and also metal nitrates the formation of expected perovskite LaCoO₃. It was also found that the losses in weight were 12.49 % and 69.10 %. Above 450 °C, there is no significant weight loss and the compound is thermally stable at that temperature. Figure 2 shows TG-DTA thermogram of dried precursor LaCoO₃ powder prepared by co-precipitation. The one endothermic peak observed at 82.14 °C and it was due to the dehydration of water. The other endothermic peak at 473 °C and it may be due to the combustion of volatile organic compound attached to the Co-OH group and the formation of expected perovskite phase.
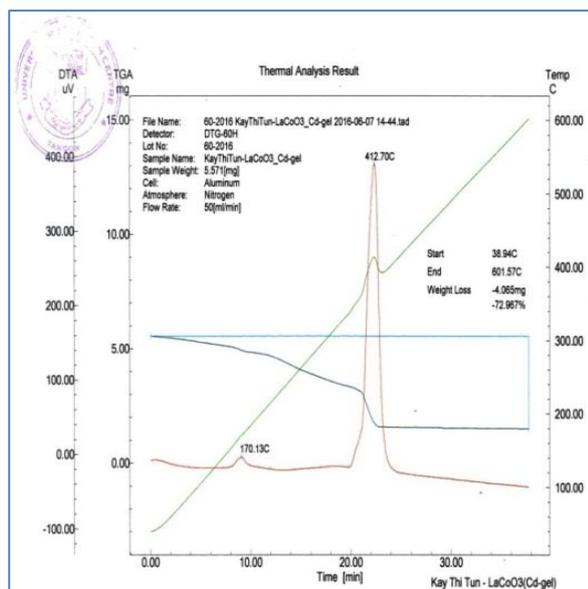
Figure 1 TG-DTA curve of the xerogel LaCoO₃ powder by citrate sol-gel method
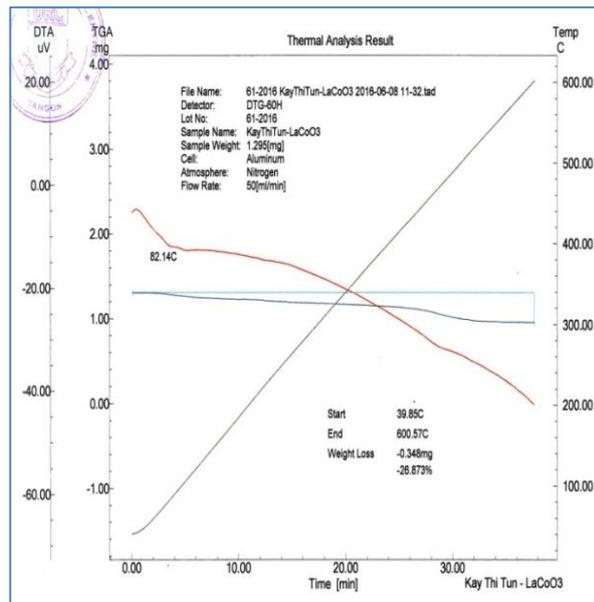
Figure 2 TG-DTA thermogram for the precursor LaCoO₃ powder prepared by co-precipitation method

XRD Analysis

XRD technique was used for the investigation of the crystalline or amorphous nature of the prepared compounds. Single phase perovskite structure was obtained after calcination at 450 °C as shows in Figure 3(a). The XRD patterns of the $LaCoO_3$ perovskite samples prepared by citrate sol-gel method sintered at different temperature ranging from 800 °C to 1000 °C for 4 h were shown in Figures 3(b). The XRD pattern of $LaCoO_3$ sintered at 800 °C shows that the formation of the mixture of $LaCoO_3$, La_2O_3, Co_3O_4 and some unidentified phase. The $LaCoO_3$ after sintering at 900 °C and 1000°C was found hexagonal crystallite structure but some higher angle lines and more crystalline nature appear at 1000 °C. The unit cell parameters of $LaCoO_3$ are found to be a= 5.44 Å, b= 5.37 Å, c= 13.09 Å at 800 °C, a= 5.37 Å, b= 5.37 Å, c= 12.94 Å at 900°C and a= 5.44 Å, b= 5.43 Å, c= 12.96 Å at 1000 °C respectively. The average particle sizes of $LaCoO_3$ are found in the range of 15-40 nm. According to XRD analysis, $LaCoO_3$ perovskite samples are well matched with standard library of ICDD-00-048-0123 hexagonal crystal structure with space group R3c. In the co-precipitation method, the perovskite crystallite structure of $LaCoO_3$ was obtained after calcination temperature at 500 °C. But there is more impurity phase on the XRD pattern; it may be due to the secondary phase of La-O and Co-O shows in Figure 4(a). The XRD patterns of the $LaCoO_3$ sintered at different temperature ranging from 900 °C, 1000°C and 1100 °C are shown in Figures 4(b). The XRD pattern of $LaCoO_3$ sintered at 900°C was aggrement with hexagonal crystallite structure of space group R3c with lattice parameters   a= 5.36 Å, b= 5.36 Å and c= 12.89 Å. The prepared $LaCoO_3$ after sintering at 1000°C and 1100 °C was found to have the same hexagonal structure but was more crystalline in nature. Aftering sintering above 900 °C showed spilliting of some higher angle lines in XRD pattern. The crystalline perovskite type $LaCoO_3$ formed at 900°C are well matched with standard library of ICDD- 00-048-0123 (Hexagonal) and the average crystallite size are found to be 36.9 nm. It shows a trend that the average crystallite size is larger at higher calcination temperature, which is related to the grain growth (Theingi, 2013) .
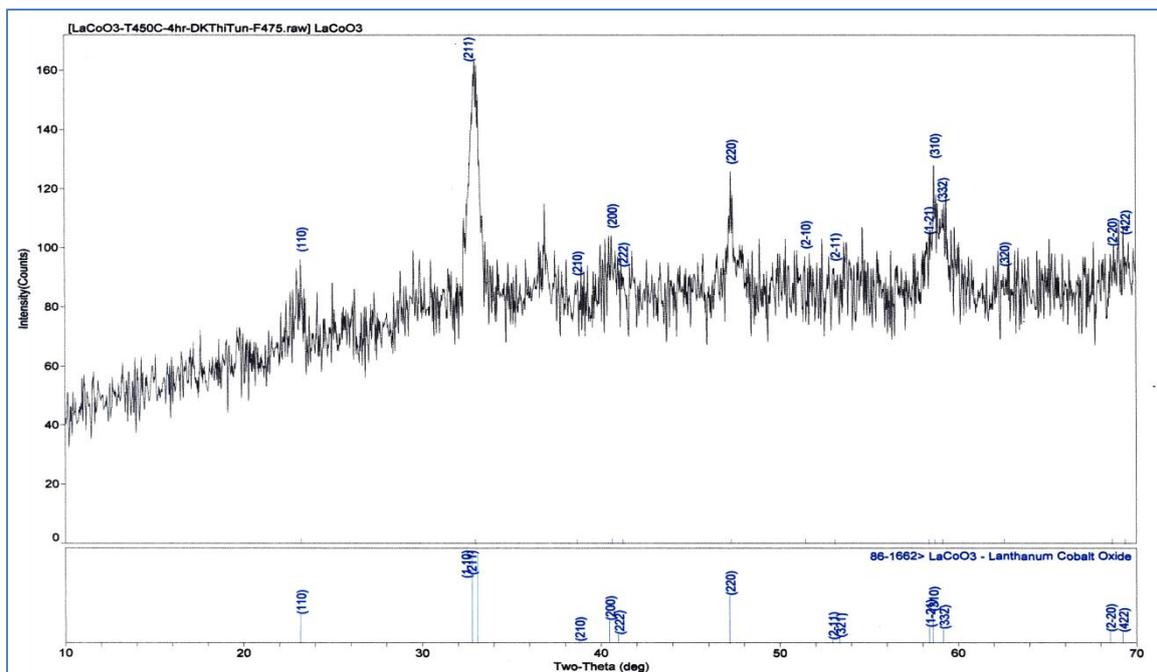
Figure 3(a) XRD diffraction pattern of LaCoO$_3$ powder prepared by citrate sol-gel method calcined at 450 °C
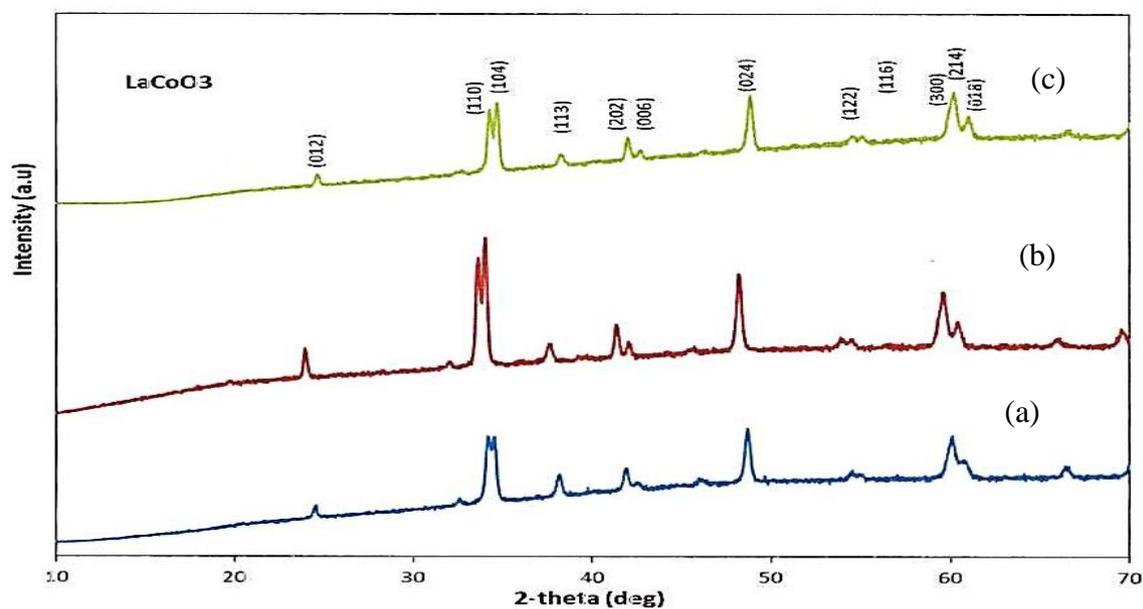
Figure 3(b) XRD diffraction pattern of LaCoO$_3$ sample prepared by citrate sol-gel method sintered at (a) 800 °C, (b) 900 °C and (c) 1000 °C
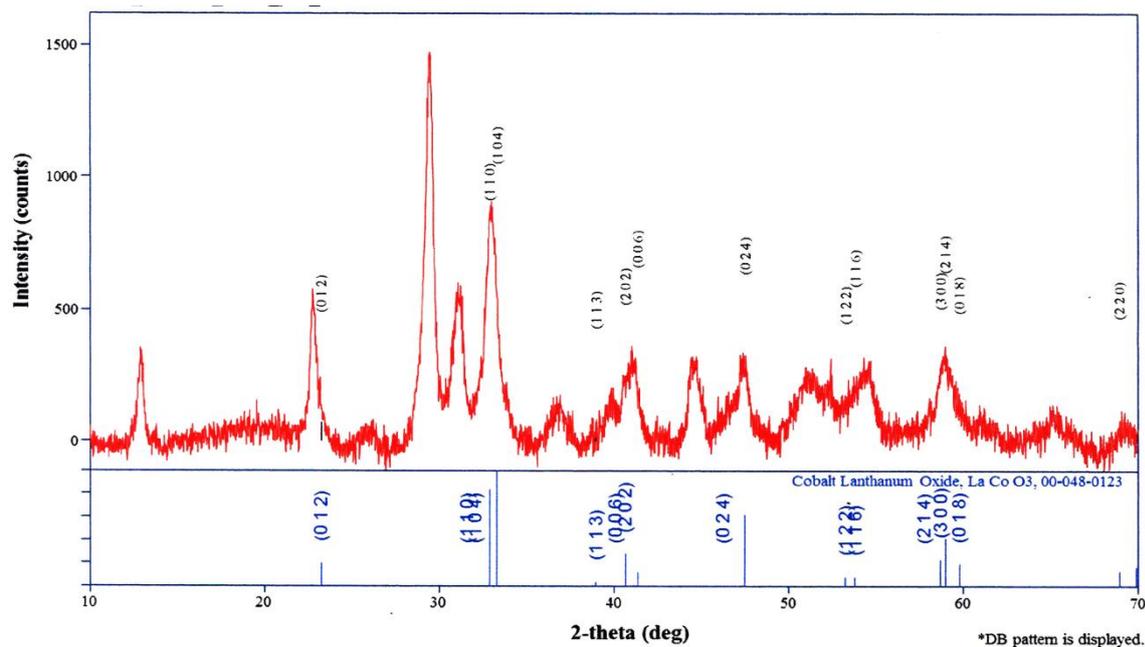
Figure 4(a) XRD diffraction patterns of LaCoO$_3$ powder prepared by co-precipitation method calcined at 500 °C
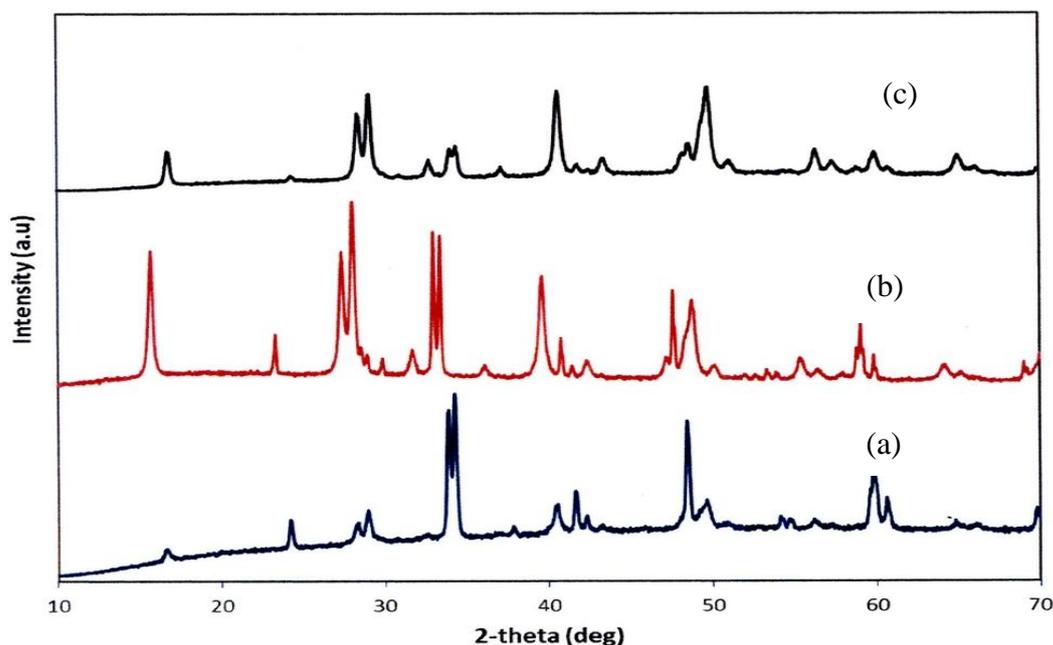
Figure 4(b) XRD diffraction patterns of LaCoO$_3$ powder prepared by co-precipitation method sintered at (a) 900 °C, (b) 1000 °C and (c) 1100 °C

FT IR Analysis

The LaCoO$_3$ nanopowders were mixed with appropiate 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 LaCoO$_3$ prepared by citrate sol-gel method and co-precipitation method, respectively. The characteristic absorption band of LaCoO$_3$ prepared by citrate sol- gel method at 665, 663 and 665 cm^{-1} at 800 °C, 900 °C and 1000 °C can be represented due to the stretching vibration of Co-O group which may be due the stretching modes

of metallic oxygen band. The Co-O stretching vibration and O-Co-O deformation modes of LaCoO$_3$ occurred at 584, 592 and 569 cm^{-1} and 406 and 414 cm^{-1} at 800 °C, 900 °C and 1000 °C can be assigned to the stretching vibration of La-O group (Ghosh and Dasgupta, 2010). It may be due to the formation of perovskite LaCoO$_3$. Compare to the citrate sol-gel method, the characteristic absorption band of LaCoO$_3$ prepared by co-precipitation method at 3603 cm^{-1} and 3171 cm^{-1} were observed at 1100 °C. It can be represented due to the stretchig vibration of OH group which may be due to the absorbed water molecules. The Co-O stretching vibration of LaCoO$_3$ occurred the absorption band at 597 cm^{-1}, 580 cm^{-1} and 642 cm^{-1} at all sintering temperatures. The band located at 420 cm^{-1}, 408 cm^{-1} and 412 cm^{-1} at 900 °C, 1000 °C and 1100 °C can be assigned to the stretching vibration of La-O group. It may be due to the formation of perovskite LaCoO$_3$ (Ghosh and Dasgupta, 2010)
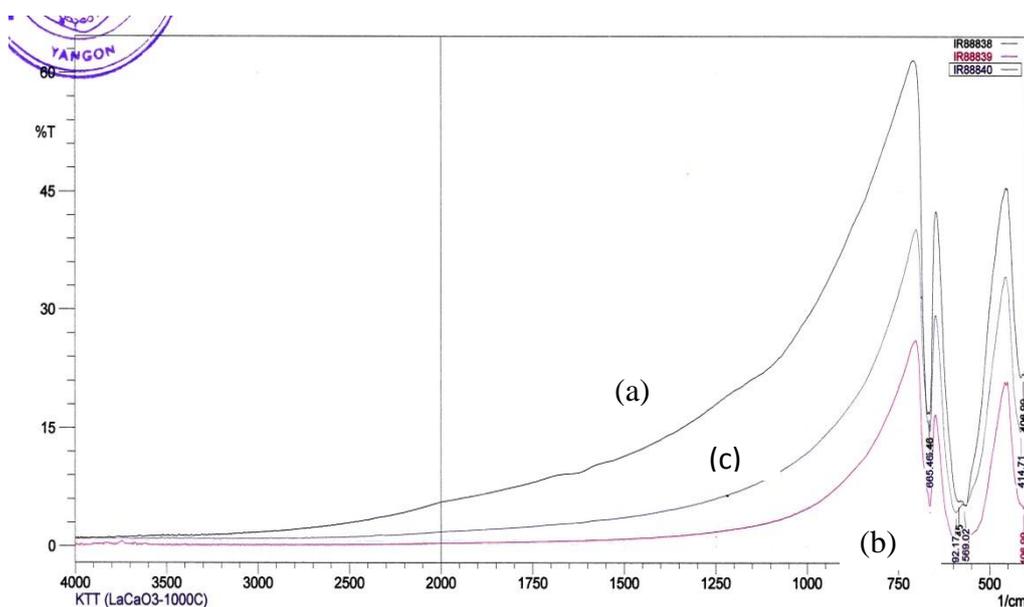
Figure 5 FT IR spectra of LaCoO$_3$ nanopowder synthesized by citrate sol-gel method sintered at (a) 800 °C, (b) 900 °C and (c) 1000 °C
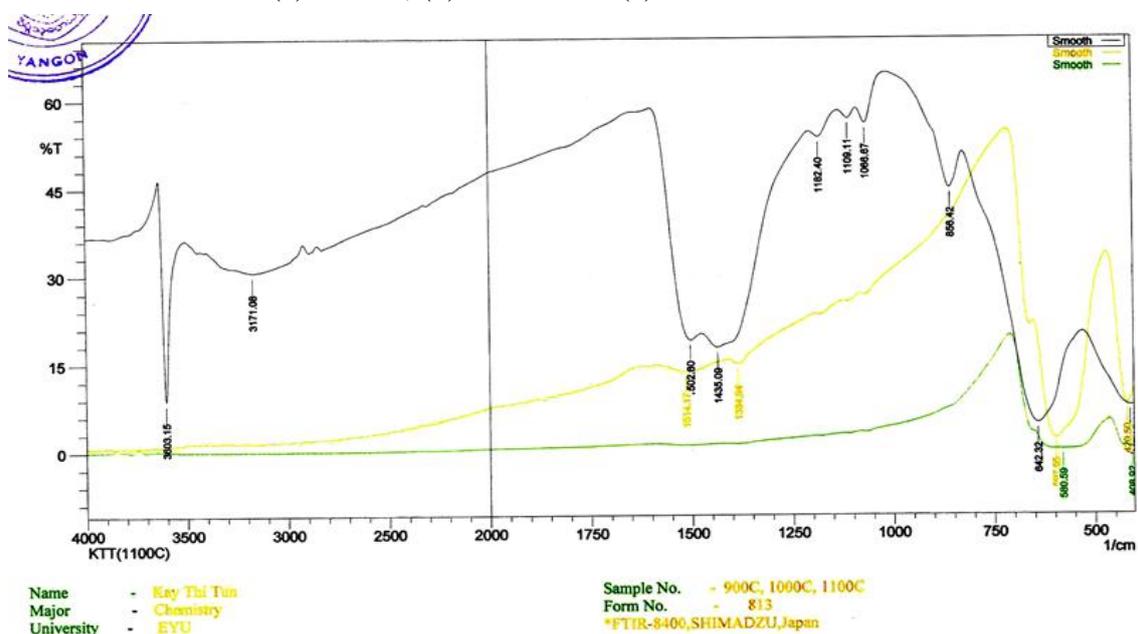
Figure 6 FT IR spectra of LaCoO$_3$ nanopowder synthesized by co-precipitation method sintered at (a) 900 °C (b) 1000 °C and (c) 1100 °C

SEM analysis

The morphology of perovskite $LaCoO_3$ sample was studied by using scanning electron microscope (SEM). The magnification of x5500 image indicates that $LaCoO_3$ prepared by citrate sol-gel method have micron size with high degree of agglomeration composed of nanocrystallite particles as shown in Figure 7. The surface morphology of perovskite $LaCoO_3$ prepared by co-precipitation method with the magnification of x30000 image indicate that $LaCoO_3$ have micron size with highly porous and uniformly distributed of nanocrystallite particles as shown in Figure8. 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).
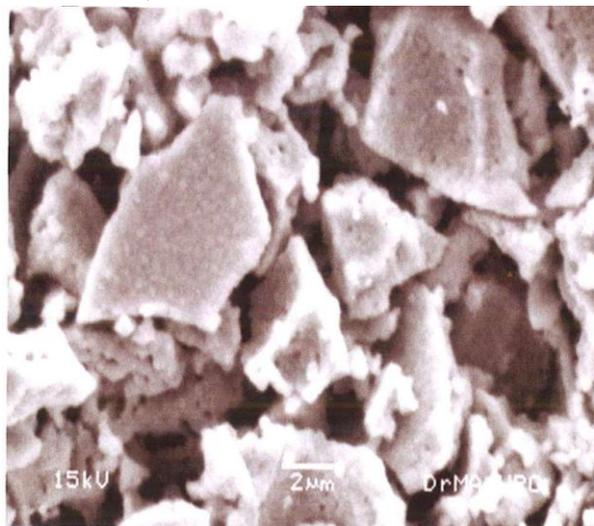
Figure 7 SEM micrograph of $LaCoO_3$ prepared by citrate sol-gel method
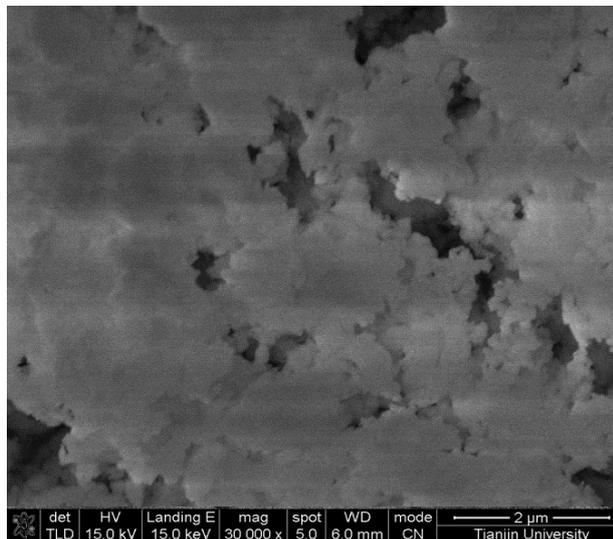
Figure 8 SEM micrograph of $LaCoO_3$ prepared by co-precipitation method

Optical Properties by UV- Vis Spectroscopy

UV-visible absorption spectroscopic method is a powerful technique to explore the optical properties of semiconducting nanoparticles. The optical properties of perovskite $LaCoO_3$ prepared by two different methods 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 $LaCoO_3$ samples were calculated from the Tauc's plots of $(\alpha h\nu)^2$ vs hν. Figures 9 and 10 show that the optical band gap of $LaCoO_3$ and it was found to be the band gap values of $LaCoO_3$ prepared by citrate sol-gel and co-precipitation methods are 2.15 eV and 2.42 eV, respectively. These band gap values are also reliable within the semiconductor band gap ranges. Band gap values of $LaCoO_3$ prepared by co-precipitation method are larger than that of the citrate sol-gel method. The prepared materials can be therefore used as gas sensor, cathode material for solid oxide fuel cell, solar cell and other optoelectronic devices.
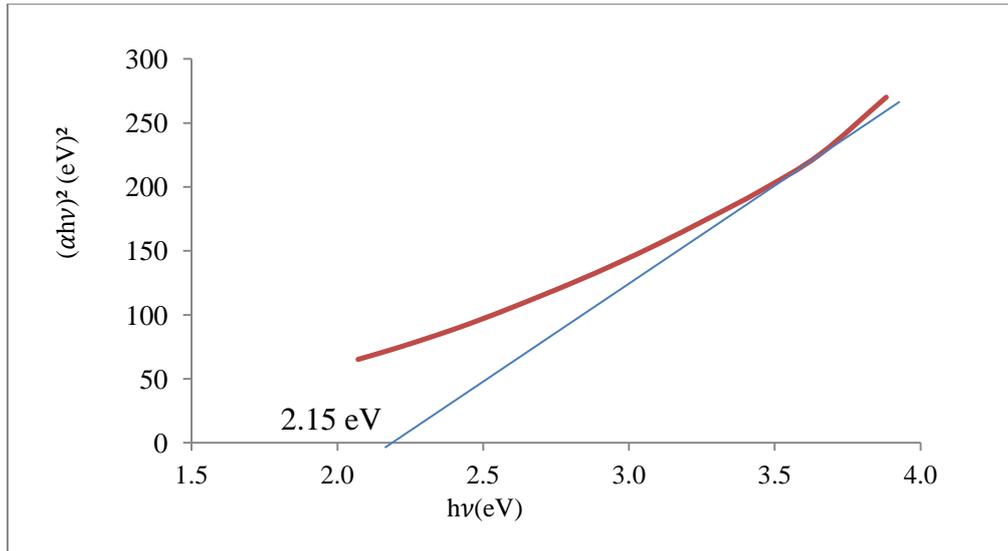
Figure 9 Plot of ($\alpha h\nu$)^2 against hν for LaCoO$_3$ prepared by citrate sol-gel method at 900 °C
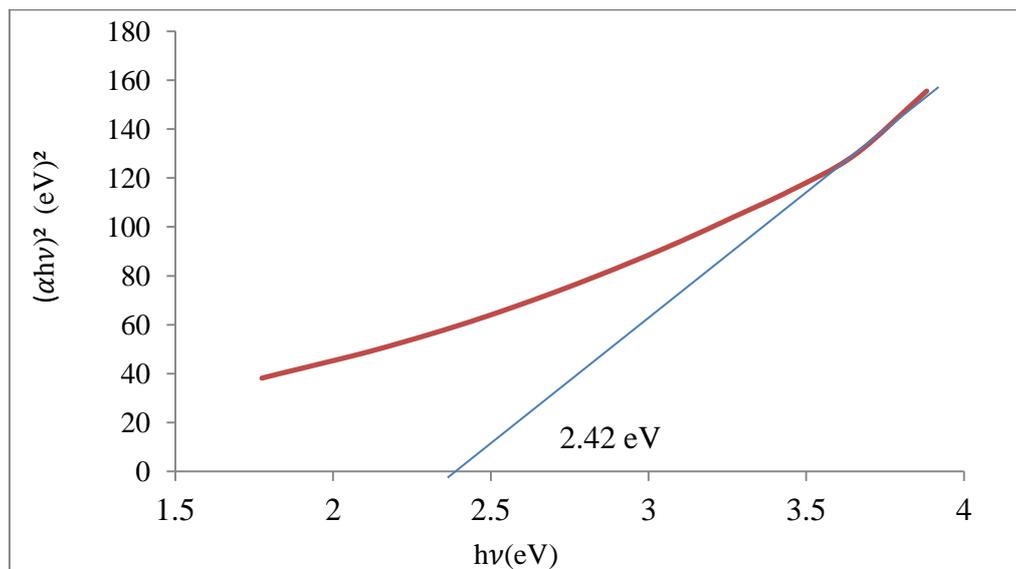
Figure 10 Plot of ($\alpha h\nu$)^2 against hν for LaCoO$_3$ prepared by co-precipitation method at 900°C

AC Electrical Conductivities

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 $\varepsilon = Cd/\varepsilon_0 A$ 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. The ac conductivity (σ_{ac}) is obtained from the data of dielectric constant (ε_0) and loss tangent (tan δ) using the relation of $\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan\delta$ where ω (2πf) is the angular frequency. Thus σ_{ac} depends strongly on the frequency of the applied field (Priyanka *et al.*, 2013). Dielectric analysis studied the electrical properties of a material as a function of frequency and measures the two fundamental electrical characteristic of materials. The first one is the capacitive nature, which represents its ability to store electric charge. The other is the conductive nature which represents its ability to transfer electronic charge. Through the analysis, the dielectric loss and dielectric constant of a material can be determined. The variation of dielectric loss and dielectric constant

of $LaCoO_3$ prepared by two different methods with frequency range from 100 kHz to 1000 kHz as shown in Figures 11 and 12. It was found that the dielectric loss and dielectric constant decrease with increase in frequency. When the frequency is increased, the orientation polarization decrease since it takes more time than electronic and ionic polarization. The value of dielectric loss and dielectric constant of $LaCoO_3$ have a constant value at higher frequency corresponding to interfacial polarization (EL-Mallah, 2012). The ac conductivity of $LaCoO_3$ prepared by two different methods increase linearly with increasing frequency and it is shown in Figure 13. The value of ac conductivity increase at higher frequency 1000 kHz (1MHz) is caused due to oxygen ion vacancy. The value of ac conductivity of $LaCoO_3$ prepared by citrate sol-gel is 8.74 $\mu\Omega cm^{-1}$ and co-precipitation method is 4.38 $\mu\Omega cm^{-1}$. It shows that the ac conductivity of $LaCoO_3$ prepared by citrate sol-gel method is greater than co-precipitation method.
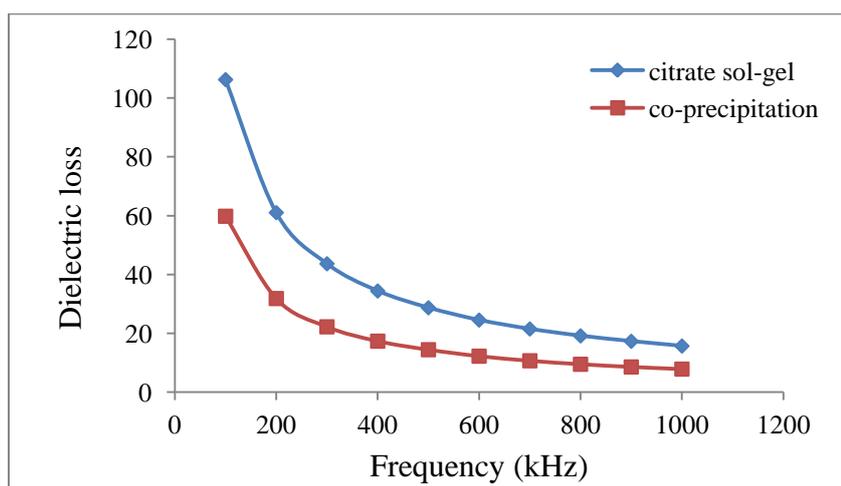
Figure 11 Variation of dielectric loss of $LaCoO_3$ prepared by citrate sol-gel method and co-precipitation method as a function of frequency
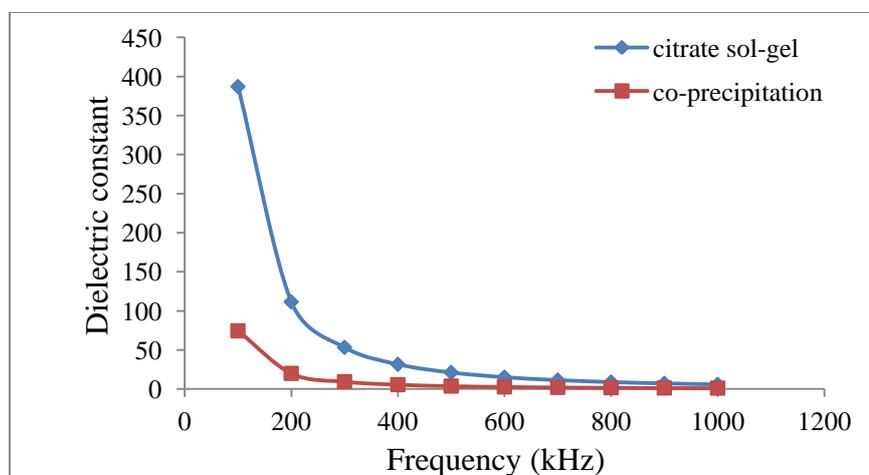
Figure 12 Variation of dielectric constant of $LaCoO_3$ prepared by citrate sol-gel method and co-precipitation method as a function of frequency
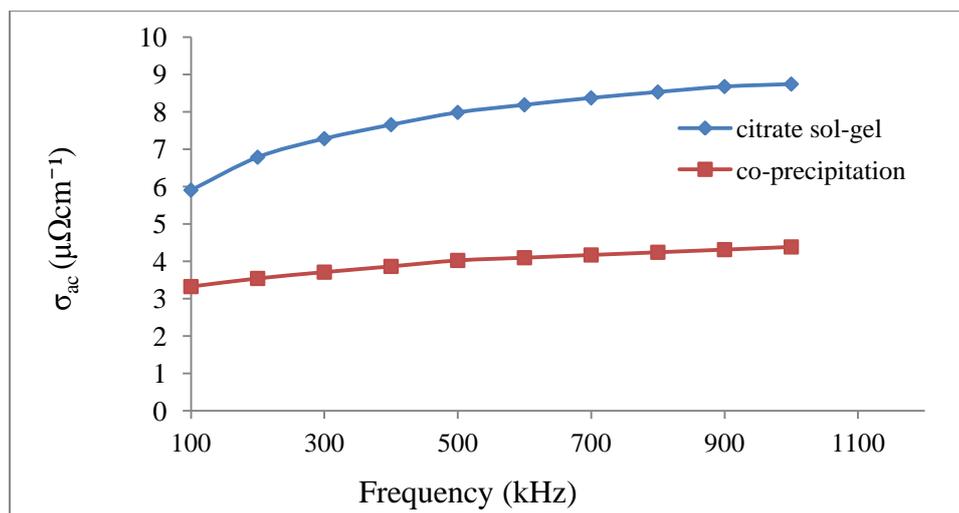
Figure 13   Variation of ac conductivity of $LaCoO_3$ prepared by citrate sol-gel method and co-precipitation method as a function of frequency

Conclusion

Perovskite $LaCoO_3$ samples have been successfully prepared by citrate sol-gel method and co-precipitation method. The different in methods lead to the difference in morphology and in electrical properties. The crystalline pellets were obtained by sintering at 900 °C and the structural, optical and ac electrical conductivities were studied. From the study of structural properties showed that the $LaCoO_3$ has hexagonal crystal symmetry with R-3c space group having crystallite size of 40.93 nm. The SEM image showed the nanostructure of the two samples. FT IR spectroscopy showed that strong absorption band appeared at 665, 592 and 406 cm^{-1} for both of citrate sol-gel and co-precipitation method and this may be due to the stretching vibration Co-O, Fe-O and La-O group. The other absorption band observed in co-precipitation method and it may be due to the presence of trace impurities. The band gap was calculated from UV-visible spectra which indicated the semiconducting nature of the materials. The optical band gap of $LaCoO_3$ prepared by citrate sol-gel and co-precipitation methods are 2.15 eV and 2.42 eV, respectively. The dielectric constant decreased in all samples with increase of frequency. The ac conductivity of $LaCoO_3$ perovskite samples were studied at the frequency range of 100-1000 kHz. The ac conductivity values of $LaCoO_3$ prepared by citrate sol-gel method are greater than the co-precipitation method. It was found that co-precipitation method required higher calcined, sintering temperatures and showed lower conductivity. These studies indicated that $LaCoO_3$ prepared by citrate sol-gel method under optimized conditions can be used as cathode material for fuel-cell technology and as touch electrode in touch sensor applications.

Acknowledgements

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