
Synthesis of High Quality LaCoO_3 Crystals Using Water Based Sol-Gel Method

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To cite this article:

Abdur Razzaque Sarker. Synthesis of High Quality LaCoO_3 Crystals Using Water Based Sol-Gel Method. *International Journal of Materials Science and Applications*. Vol. 4, No. 3, 2015, pp. 159-164. doi: 10.11648/j.ijmsa.20150403.13

Abstract: Lanthanum cobaltite (LaCoO_3) crystalline material is a promising material for its interesting electrical, magnetic, catalytic and thermoelectric properties. In this study, LaCoO_3 powders were synthesized by water based sol-gel method using metal nitrates as precursors and citric acid as the chelating agent at room temperature. The dried powders were amorphous and their thermal decomposition occurs stepwise upon heating to 400 °C. Pure perovskite-type single phase LaCoO_3 polycrystals are formed after heating at 600 °C. The pellets prepared from calcined powders were sintered at 1200 °C and crystalline pellets were characterized for investigation of electrical, optical and thermoelectric properties. The obtained results revealed that the prepared samples were highly crystalline with large cation ordering. The sol-gel method found to be efficient for much production of a lot of crystalline transition metal oxides at low cost.

Keywords: Ceramics, Heat Treatment, Sol-Gel Method, Powder Diffraction, Optical Properties

1. Introduction

The urgent important issue for development of environment is to control automobile and industrial emission of toxic gases by using the catalytic converters. Lanthanum cobaltite (LaCoO_3) is one of the most promising catalytic materials that have many practical applications for its excellent physical and chemical properties [1]. This catalyst can be used for combustion, automobile exhaust and waste gas purification. Moreover, it can be used as an electrode material for solid-state fuel cells, gas sensors [2] and thermoelectric power production for its excellent thermoelectric properties. The properties of the produced material strongly depend on the method of preparation. During the preparation, it is essential to control the synthesis of homogeneous, highly pure and high surface area LaCoO_3 materials.

The LaCoO_3 materials have been synthesized by several techniques such as solid-state reaction, sol-gel, solid-state thermal decomposition, flame hydrolysis and electrochemical oxidation methods. These processes are generally complicated and the reagents used are very expensive except sol-gel method [3]. Sol-gel process has some potential advantages over other methods such as the homogeneous mixing of the components at the atomic scale. The sol-gel method using a

chelating agent like citric acid is considered a useful technique because it presents the advantages of allowing a good stoichiometric control, obtaining good particle size distributions, low temperature and short periods of calcinations [4].

The cobalt contained perovskites are potential candidates for cathode materials of solid oxide fuel cells (SOFCs) due to their high electrical and ionic conductivities and their excellent electrochemical properties [5]. For SOFCs electrodes and oxygen separation membranes both electronic and ionic conductivities should be as high as possible [6]. Thermoelectric energy conversion is a promising technology for both electrical power generation from waste heat and various electronic cooling devices. Cobalt oxides are of particular interest as the thermoelectric materials because of its large Seebeck coefficient and semiconducting or metallic electric conductivity [7]. They exhibit a strongly correlated electron system with Co ions presenting an energy level degeneracy of electron states, which are considered as the origin of the large Seebeck coefficient at low temperatures [8]. The optical properties of LaCoO_3 perovskites were not studied in details experimentally and theoretically. In this work, we try to prepare the ceramics of LaCoO_3 by water based sol-gel method from non-alkoxide precursors and citric acid as a chelating agent for characterizations and investigation of the

electronic, optical and thermoelectric properties.

2. Experiment

The composition of the starting solutions were $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, which were weighted in equimolar amounts and dissolved in distilled water (0.2 M). Citric acid as chelating agent was added to this solution after 10 minutes of mixing in molar ratios of citric acid/total cations of one. The resulted solution was stirred at room temperature for 3 h leading to a red transparent solution. The solutions were kept at 80 °C for 24 h and amorphous gels were obtained. The gels were thermally treated in air at 600 °C for 6 h. The heating rate was 1 °C/min up to 400 °C and 5 °C/min up to 600 °C. The thermal behavior of samples was determined by TG/DTA by using TG/DTA630 in Al_2O_3 crucibles and in air atmosphere. The maximum temperature was set at 750 °C and the heating rate was 5 °C/min. The annealed powder samples were evaluated by X-ray diffraction using a CuK_α ($\lambda=0.154$ nm) radiation source in a BRUKER D 8-Discover X-ray diffractometer. The diffraction angles (2θ) range between 5° and 80° was scanned.

From the calcinated powders pallets with 10 mm diameter and height of 2 mm were made by uni-axial pressing under 60 MPa, without any binding materials. The obtained pallets were sintered at 1200 °C for 12 h soaking time. Mirror like polishing was done for the disc like samples. The surface of the samples was analyzed by Atomic force microscope (AFM). The Agilent 4294A Precision Impedance Analyzer (Agilent technologies, Model: 4294A Japan) was used for measurements of frequency dependences conductance, impedance, dielectric constant and capacitance. Fourier transform infrared (FTIR) spectrophotometer (Spectrum 100, Perkin Elmer) was used for FTIR transmission spectrum of the powder samples. The samples were characterized by UV-Visible spectrophotometer (Shimadzu: UV-1650 PC) for wavelength dependence absorption spectrum. The temperature dependence electrical resistivity was measured using two-probe technique.

3. Results and Discussions

The gels obtained after heating the solution at 80 °C was red in color. The dried gels were amorphous as determine by XRD. The thermal decomposition of the powder after drying the gel is presented in Fig.1. The dried precursors lose weight stepwise. After 400 °C there is no pronounced weight loss. On the differential thermal analysis (DTA) curve, a strong exothermic effect in the range 315 – 375 °C, with maximum at ~342 °C is observed indicating that the thermal events can be primarily associated with the nitrate decomposition and the burn out of organic species in the powder or due to direct crystallization of LaCoO_3 from the amorphous component. Based on the TG/DTA results, the dried gels were annealed up to 600 °C as mentioned in the experimental section.

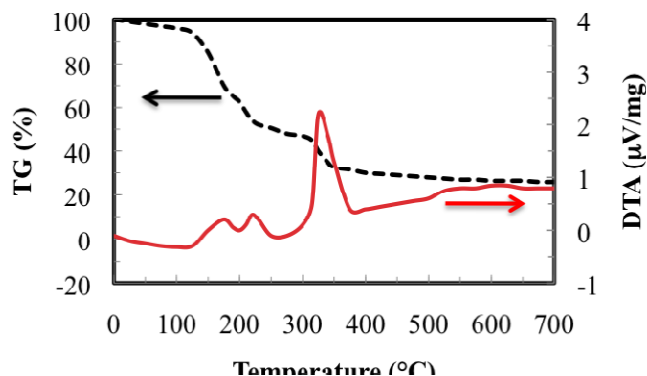


Figure 1. The TG/DTA curves of the thermal decomposition of LaCoO_3 sample.

The XRD data of the thermally treated gels are presented in Fig.2. Except the data presented by Popa *et. al.* [9], this is the lowest temperature mentioned in the literature, for pure LaCoO_3 phase formation. Almost complete crystallization of LaCoO_3 powders takes place before 700 °C. The pure perovskite-type lanthanum cobalt oxide was obtained when gels were thermally treated at 600 °C for 6 h. The powder samples were characterized at room temperature by an X-ray diffractometer range from $2\theta = 5^\circ$ to 80° with CuK_α radiation ($\lambda=1.5418$ Å), at 40 KV and 30 mA. The unit cell refinement was accomplished using XRD data and CellCal software. Typical XRD patterns of LaCoO_3 crystalline powers shown in Fig.2 reveals that prepared samples are single phase with trigonal crystal structure of rhombohedral symmetry, space group R3c (167). The prepared samples were identified as

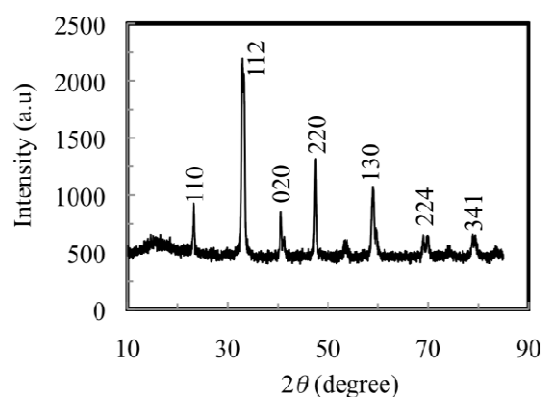


Figure. 2. X-ray diffraction pattern of the LaCoO_3 sample annealed at 600 °C.

highly crystalline and homogeneous by indexing these XRD patterns using JCPDS data No. 25–1060. Here sharp peaks indicate the good crystallinity. In the XRD pattern the impurity phase peaks of La_2O_3 , Co_3O_4 or CoO are absent, so the pure phase powder was obtained, which indicates that LaCoO_3 can be synthesized fast by sol-gel method. The good crystallinity of the LaCoO_3 crystals would improve the efficiency of devices such as SOFCs. Reported structural parameters of LaCoO_3 crystals derived from XRD data are shown in the Table I. In this work the crystal structure, lattice constants, cell volume and band gaps are consistent with

reported values [10 – 13]. In the XRD patterns, (112) peaks indicates the property of layer structure of LaCoO₃ crystals and (220) peaks indicates the property of basic unit of

Co-O-Co bond which form this kind of layer compound, and the intensity ratio of (112) and (220) peaks indicates the perfection of crystallization.

Table 1. Structural parameters of LaCoO₃ derived from X-ray diffraction data and comparison with other reported values.

Crystal structure	Lattice parameter	Unit cell volume (Å ³)	Band gap (eV) and conductivity	Reference
Trigonal structure with rhombohedral symmetry	$a = b = c = 4.30 \text{ Å}$ $\alpha = \beta = \gamma = 60.48^\circ$	114.88	$E_g = 1.0 \text{ eV}$ Semiconductor	[10]
Trigonal structure with hexagonal symmetry	$a = b = 5.4036 \text{ Å}$ $c = 13.312 \text{ Å}$ $\alpha = \beta = \gamma = 60.48^\circ$	336.978	$E_g = 1.2 \text{ eV}$ Semiconductor	[11]
Trigonal structure with rhombohedral symmetry	$a = b = c = 5.377 \text{ Å}$ $\alpha = \beta = \gamma = 60.79^\circ$	111.955	$E_g = 1.0 \text{ eV}$ Semiconductor	[12]
Trigonal structure with rhombohedral symmetry	$a = b = c = 5.370 \text{ Å}$ $\alpha = \beta = \gamma = 60.79^\circ$	111.449	$E_g = 1.0 \text{ eV}$ Semiconductor	[13]
Trigonal structure with rhombohedral symmetry	$a = b = c = 5.432 \text{ Å}$ $\alpha = \beta = \gamma = 59.76^\circ$	112.726	$E_g = 1.1 \text{ eV}$ Semiconductor	This work

The cation ordering in the crystal structure of cathode material is one of the most important factors for good performance that is measured by the intensity ratio of the main peaks in the XRD patterns. It has been proposed that the electrochemical performance of LaCoO₃ cathode material is remarkably improved when the (112)/(220) peaks intensity ratio is higher than 1.2 [9]. The reported intensity ratios of main peaks of LaCoO₃ crystals are shown in the Table 2 that reveals the crystallinity and cation ordering is higher in case of solid-state reaction synthesis by S. Sompech *et al.* [1]. In this work that ratio was 1.67 that is higher than other reported values. This suggests that high quality LaCoO₃ crystals might be synthesized by water based sol-gel method using low capital cost.

Table 2. Intensity ratio of the largest two peaks, grain size, defect density and micro strain derived from X-ray diffraction data and comparison with other reported values.

I_{112}/I_{220}	D (nm)	$\delta \times 10^{-3}$ (lines/m ²)	$\epsilon \times 10^{-3}$ (lines ² .m ⁴)	Reference
1.826	62.83	2.533	2.04	[1]
1.069	21.767	21.11	4.11	[5]
1.2	13.382	55.84	4.82	[15]
1.171	16.261	37.96	7.80	[16]
1.667	21.88	20.80	5.88	This work

The performance of LaCoO₃ crystals in SOFCs or other device applications is affected by a numerous factors such as anode and cathode particle size (D), micro strain (ϵ), and dislocation density (δ) [17]. The average grain size (D) and micro strain (ϵ) of the LaCoO₃ crystalline powder were calculated using Scherrer formulae, $D = \frac{0.94\lambda}{\beta \cos \theta}$ and

$\epsilon = \frac{\beta}{4 \tan \theta}$, respectively [18], where λ is the X-ray wavelength (1.5418 Å), 0.94 is the crystal shape constant, θ is the reflection angle of the highest peak and β is the full width at half maximum (FWHM) of the highest peak in radians. The dislocation density (δ) of the LaCoO₃ crystalline powder was estimated using the equation $\delta = \frac{1}{D^2}$ (lines/m²) [18]. The

calculated D , δ and ϵ values are listed in Table 2. The obtained values are comparable to the reported results [1, 5, 15, 16].

The crystallinity of LaCoO₃ grown by S. Sompech *et al.* is very high whereas average grain size is very large in comparison of other reported values. The dislocation density (δ) indicates the length of dislocation lines per unit volume and measures the amount of defects in a crystal. On the other hand micro strain (ϵ) measures the strain per unit volume square. Both the values of δ and ϵ reported to be lower among other presented data. It means that the quality of the lanthanum cobaltite grown by sol-gel method is high.

FTIR spectroscopic results are shown in the Fig.3 that confirm the XRD data showing that the vibration bands for precursors vanished and the vibration bands for the oxide network developed. The FTIR spectrum of LaCoO₃ powder has three characteristics bands at 423 cm⁻¹, 590 cm⁻¹, and 597 cm⁻¹ that ascribed to the vibration of metal oxygen band, indicating that LaCoO₃ was formed. La – O was assigned to the presence of the absorption band at 423 cm⁻¹ [14]. The strong absorption bands at 590 and 597 cm⁻¹ are assigned to Co – O stretching vibration and O – Co – O deformation modes of LaCoO₃, respectively. There are three sharp medium absorption peaks at 1384 cm⁻¹, 1497 cm⁻¹ and 1627 cm⁻¹, which are all due to the vibrations of the lanthanum cobaltite crystal lattice. The results of FTIR analysis were good agreement with XRD results.

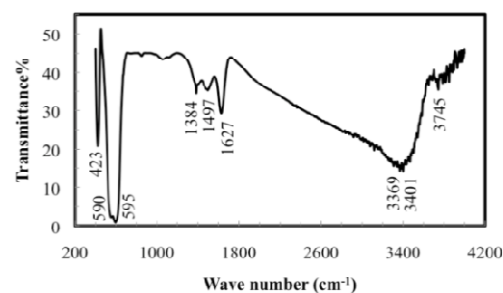


Figure 3. FTIR spectrum of LaCoO₃ sample.

The a-c conductivity was measured by impedance analyzer, frequency was varied from 100 Hz to 10 M Hz and oscillating voltage was 300 mV. Fig. 4(a) shows the frequency dependence a-c conductivity of LaCoO₃ where conductivity increases with frequency. The impedance was also measured

at frequency range 100 Hz to 10 MHz by impedance analyzer. Fig. 4(b) shows the frequency dependence impedance of LaCoO_3 sample.

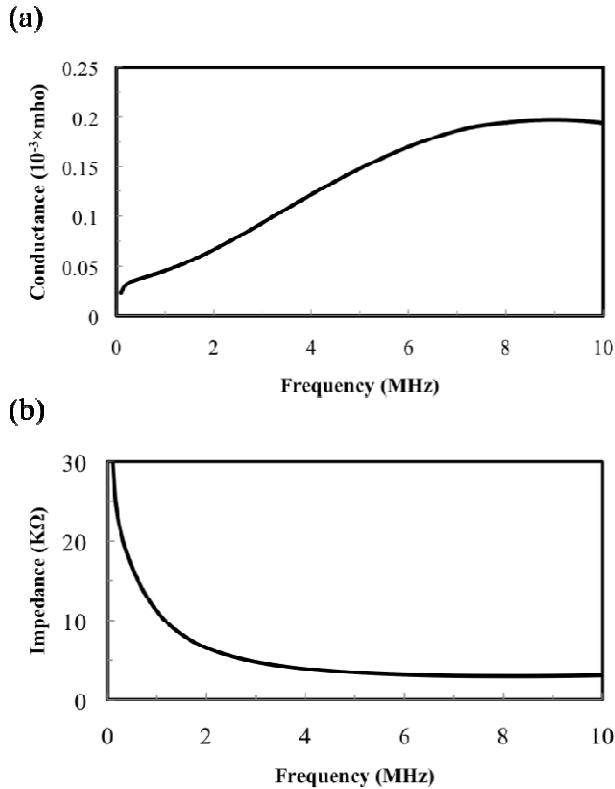


Figure 4. The plot for frequency dependence of (a) electrical conductivity and (b) impedance of LaCoO_3 sample.

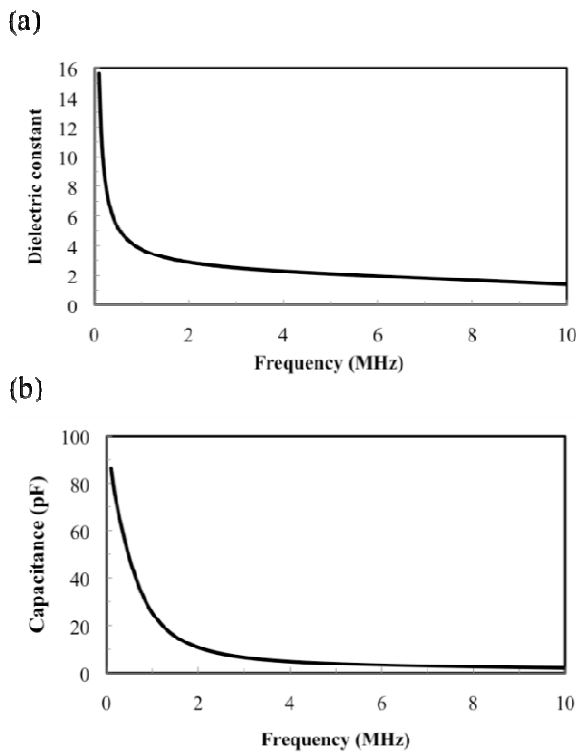


Figure 5. The plot for frequency dependence of (a) capacitance and (b) dielectric constant of LaCoO_3 sample.

Dielectric properties of the prepared LaCoO_3 samples were studied by precision impedance analyzer. Silver paste was coated on both surface of each sample before measurement. Dielectric constant is a measure of materials ability to store electric charge. The frequency dependence capacitance of sample was measured within the frequency range 100 Hz to 10 MHz at room temperature as shown in Fig. 5(a). The capacitance of LaCoO_3 is high at low frequency region and decreases with increase of frequency. Fig. 5(b) shows the frequency dependence dielectric constant of LaCoO_3 sample. The capacitance of LaCoO_3 is high at low frequency region due to contribution of all kinds of polarization at low frequency, then decreases with increase of frequency and finally approaches to all most constant value above 5 MHz. This is due to the change of space charge, ionic and orientation polarization at higher frequencies [19].

The UV-Visible absorption spectrum of the sample was recorded by using a UV-Vis spectrophotometer (Shimadzu: UV-1650 PC) in the photon wavelength range between 200 – 800 nm. Fig.7 Show the absorption spectrum of LaCoO_3 sample. The absorption increases with increase of wavelength from ultraviolet to visible. This change is exponential in the edge and tail regions. There is an absorption peak in 348 nm that is the region of violet. The nature of exponential edge and tails may be associated with localized energy states in the band gap. This result shows that our data is consistent with interpretation that the exponential optical absorption edge and the optical band gap are controlled by structural defects in the LaCoO_3 . This phenomenon showing good optical quality is in good agreement with the data reported by others [20].

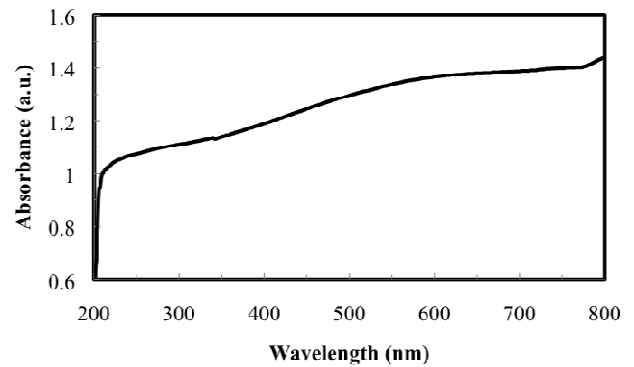


Figure 6. The UV-Vis absorption spectrum of LaCoO_3 crystals.

LaCoO_3 oxide is one of the most promising p-type thermoelectric oxides. The energy conversion efficiency of a thermoelectric device is mainly determined by the figure of merit (ZT) of its corresponding materials, which is expressed as $ZT = S^2 T / \rho \kappa$, where S , ρ , κ and T are Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively. Therefore, good thermoelectric materials with a high ZT should have a low electrical resistivity ρ , a high Seebeck coefficient S , and a low thermal conductivity κ . We measured the electrical resistivity, ρ of the LaCoO_3 sample at room temperature to 513 K as shown in Fig. 7 . The electrical resistivity decreases with increasing

temperature. We also calculated the thermal conductivity, κ using Wiedemann-Franz law. We calculated the Seebeck coefficient, S at the crossing point of ρ and κ using the standard value of $ZT = 0.2$ reported by Robert et al. [21]. The calculated Seebeck coefficient is 149.6 mVK^{-1} that is large among the reported values.

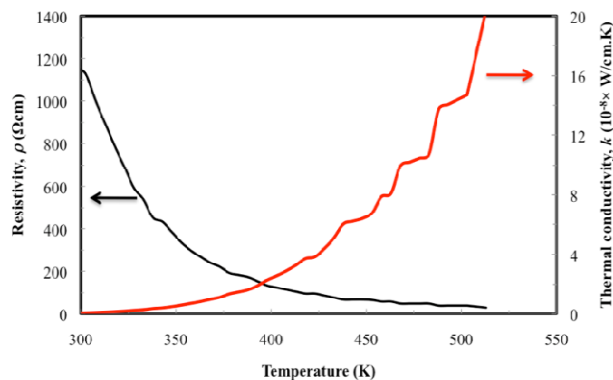


Figure 7. The plot for temperature dependence of (a) electrical resistivity and (b) thermal conductivity of LaCoO_3 crystal.

Cobalt oxide thermoelectric materials are relatively stable at high temperatures and receive recent attention in the fields of energy conversion [22]. They exhibit a strongly correlated electron system with Co ions presenting an energy level degeneracy of electronic states, which are considered as the origin of the large Seebeck coefficient at low temperatures. Lanthanum cobalt oxide (LaCoO_3) with a rhombohedral distorted perovskite structure provides a typical example for the thermally assisted spin state transition of the trivalent cobalt [8].

4. Conclusion

LaCoO_3 single-phase powders have been successfully prepared by water based sol-gel route using nitrate precursors and pure LaCoO_3 perovskite-type polycrystals were obtained after calcinated at 600°C . Dense crystalline pellets were obtained by sintering at 1200°C and its electrical, optical and thermoelectric properties were studied. From structural properties and crystal quality studies, it has been assessed that high quality LaCoO_3 was successfully synthesized. The structural and optical measurements reveal that the grown samples are crystalline and its optical properties are well agreements with literature. The electrical properties of the samples investigated by impedance spectroscopy are also well agreement with literature. The ZT values were not increased at elevated temperatures as the thermal conductivity increases apparently with temperature. This result reveals an intrinsic correlation between transport behavior and thermoelectric response. The thermoelectric properties might be improved by choosing suitable substitution with a proper doping content and by controlling the crystal structure factors in such a strongly correlated electron system with transition metals that study is our next attempt.

Acknowledgements

This work was partially supported by the Rajshahi University Research Grant (No. A 774). Authors would like to thanks Rajshahi University, Rajshahi, Bangladesh authority for providing funds under the University Research Project to carry out this work. The authors thank Mr. Md. Saiful Islam, Senior scientific officer, Cetral science laboratory, Rajshahi university for providing the experimental facilities.

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