Structural and Electrical Properties of Barium Strontium Cobaltite Nanoparticles Synthesized by Wet Chemical Methods

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Abstract. Barium strontium cobaltite (Ba\textsubscript{0.5}Sr\textsubscript{0.5}CoO\textsubscript{3-δ}) nanoparticles were synthesized without water and surfactant (WOWS) sol-gel method, co-precipitation method and composite mediated hydrothermal method (CMHM). Co-precipitation synthesis was carried out for 0.4 M solutions of strontium nitrate Sr(NO\textsubscript{3})\textsubscript{2}, cobalt nitrate hexahydrate Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and barium nitrate Ba(NO\textsubscript{3})\textsubscript{2} with the sodium hydroxide NaOH as precipitating agent. Sol-gel synthesis was done using ethylene glycol as precipitating agent and the CMHM synthesis was done using sodium hydroxide and Potassium hydroxide (NaOH-KOH) as reactants and precipitating agents at 180 °C for 65 min. Calcination of the synthesized samples was done at 830 °C for 02 hours. Pellets of calcined powder were sintered at 850 °C for 20 minutes. X-ray diffraction (XRD) study was used to find the structural parameters (crystal structure, crystallite size and phase purity). The observed phase transformation of pure barium strontium cobaltite monoclinic to orthorhombic structure was found after heat treatment. Crystallite sizes were calculated by using Scherrer’s formula. Temperature dependent (100 to 600 °C) DC conductivities of the sintered pellets were increased with the increase of measuring temperature. Temperature dependent (100 to 600 °C) impedances of all samples synthesized through wet chemical methods at fixed frequency of (10kHz) were also measured and compared. The structural and AC/DC electrical properties were correlated to different synthesis methods. The synthesized samples can be thought as an electrode material for intermediate temperature range solid oxide fuel cells (IT-SOFCs).

Introduction

Perovskite based oxides ABO\textsubscript{3-δ} materials have an ability to manage range of oxygen vacancies. Moreover, it has mixed oxidation states of transition metal atom at B site. Usually A site contains metal ions having lower valency that in turns produces oxygen vacancies. These oxygen ions vacancies are responsible for oxygen ion conduction. B site contains metal ions of variable oxidation state. The hoping of electrons of B site metal ions causes electronic conductivity [1]. Strontium cobaltite (SrCoO\textsubscript{3-δ}) is an important parent compound of perovskite family. It is a promising material of mixed electronic-ionic conductivity [2]. Strontium cobaltite has found wide spread applications such as combustion catalyst, oxygen separation membrane and as an electrode material for solid oxide fuel cell [3]. Strontium cobaltite shows orthorhombic brownmillerite or hexagonal 2H-type structure at low temperatures and cubic perovskite structure at high temperatures. Cubic perovskite structure has mixed maximum electronic, oxygen ionic conductivity of 160Scm\textsuperscript{-1} at 950°C [4]. The total electrical conductivity of all other phases of strontium cobaltite was lower than the cubic phase. The stability of cubic phase of strontium cobaltite can be enhanced by doping either at A site or at B site [5-7]. For cubic perovskite structure, the most stable oxidation state is Co\textsuperscript{3+}. But with this oxidation state the size of A-site cation (Sr\textsuperscript{2+}) is very small to withstand a stable cubic perovskite structure. Therefore, Shao proposed partial substitution of large size alkaline earth cation barium (Ba\textsuperscript{2+}) with strontium (Sr\textsuperscript{2+}) to increase the stability of perovskite structure. According to his calculation, substitution of 50% strontium (Sr\textsuperscript{2+}) by barium (Ba\textsuperscript{2+}) may produce a stable perovskite structure. Beside this, barium (Ba\textsuperscript{2+}) substituted strontium cobaltite (SrCoO\textsubscript{3-δ}) may possesses maximum oxygen vacancy concertation [1,8,9]. In another study, barium
and iron substituted strontium cobaltite materials have excellent properties towards cathodes of IT-SOFCs [10].

Present work focuses on the correlation between structural properties and electrical performance of the barium (Ba) doped strontium cobaltite perovskite oxide system. Moreover, effects of synthesis methods WOVS Sol-gel, CMHM and co-precipitation method on structural properties was done which has not been reported so far to the best of our information. Wet chemical methods used in this work for synthesis because of their ability towards good physical and chemical homogeneity of synthesized materials [11].

Also, DC electrical conductivity and AC impedance of the samples synthesized by three different methods were measured as a function of temperature (100-600 °C) at a fixed frequency (10 kHz) respectively. DC conductivities showed increasing trend while the AC impedances decreased with increasing temperature.

**Experimental Details**

Barium strontium cobaltite nanoparticles were synthesized using WOVS sol-gel, CMHM and co-precipitation method. Barium nitrate \( \text{Ba(NO}_3\text{)}_2 \) (Fisher Scientific), Strontium nitrate \( \text{Sr(NO}_3\text{)}_2 \) (Sigma-Aldrich) and cobalt nitrate hexahydrate \( \text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (Panreac Quimica Sau) were used for the synthesis of barium strontium cobaltite samples.

In co-precipitation method, synthesis was done by 0.4 M solutions of precursors formed in deionized water. All the 0.4 M solutions of the precursors were mixed with continuous stirring to make a homogenous solution. 2.0 M solution of sodium hydroxide (NaOH) was used as a precipitating agent. The temperature of the solution was maintained at 70 °C under continuous stirring. The pH of the solution was maintained at 8.5. Finally, the formed precipitates were washed with deionized water to remove the by-products. The synthesized sample was dried in an electric oven at a temperature of 105 °C. The sample was grinded to fine powder and calcined at 830 °C for 2 h. Calcined powder was pelletised to a diameter of 10 mm and sintered at 850 °C for 20 minutes.

WOVS sol-gel method synthesis was done by all the same precursors used in co-precipitation method using ethylene glycol (1:14) as gelatinising agent. All precursors were dissolved in ethylene glycol with constant stirring at room temperature. When homogenous solution was formed then the temperature of the solution was increased to 80 °C for 2 hours. After 02 hours, the formed gel was heated up to a temperature of 200 °C successively. Finally, the gel was burnt to fine powder. Calcination of the powder was done at 830 °C for 2 h and calcined powder was used to make pellets of 12 mm diameter. Sintering of pellets was done at 850 °C for 20 minutes.

Composite mediated hydrothermal synthesis was done using the sodium hydroxide and potassium hydroxide (NaOH-KOH) as precipitating agents. For the molar ratio of 0.515:0.485 NaOH-KOH system, the eutectic point is 170 °C [12]. Precursors were finely grinded, mixed and put in a Teflon vessel. Then the vessel was placed in a pre-heated oven maintained at a temperature of 180 °C for 65 min. The contents of the vessel were removed after it reached at room temperature. All the contents of the vessel were washed several times to remove the water-soluble impurities with de-ionized water. Washed sample was dried at 105 °C overnight. Finally, the powder was calcined at 830 °C for 2 h. Calcined powder was used to make pellets of 13 mm diameter. Sintering of pellets was done at 850 °C for 20 minutes.

**Results and Discussion**

**Structural analysis (X-ray Diffraction).** Crystal structure and average crystallite size \(<D>\) of the prepared samples were calculated on Pan Analytical Xpert Pro diffractometer. The scanning of samples for range 20-80° was done by using Cu Kα radiation. Scherer formula (Eq. 1) was used to estimate the crystallite sizes \(<D>:\)

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]  
(1)
where \( k \) in the equation is called shape constant whose value is 0.9, \( \lambda \) is the wavelength of X-ray source [1.54 Å], \( \beta \) is full width at half maximum (FWHM), and \( \theta \) is Bragg’s angle. The lattice cell parameters \( a, b, \) and \( c \) of the monoclinic, orthorhombic and hexagonal system were measured using the check cell software. Figures 1 and 2 show the indexed XRD patterns of the as-prepared and sintered samples synthesized by three different methods respectively.

![Fig. 1. XRD pattern of Ba\(_{0.5}\)Sr\(_{0.5}\)CoO\(_{3-\delta}\) as-prepared samples synthesized by CMHM, Co-precipitation method and WOWS sol-gel method.](image1)

![Fig. 2. XRD pattern of Ba\(_{0.5}\)Sr\(_{0.5}\)CoO\(_{3-\delta}\) sintered at 850 °C synthesized by CMHM, Co-precipitation method and WOWS sol-gel method.](image2)

In hydrothermally as prepared samples, orthorhombic structure was found with a small percentage (25 %) of barium nitrate (Ba(NO\(_3\))\(_2\)) as shown in table 1. After calcination at 830 °C, almost-phase pure crystal structure (JCPD card no. 01-083-0377) was formed. After heat treatment (calcination, sintering), crystallite size, lattice parameters, and cell volume were also changed as shown in Table 1. After calcination and sintering of the samples, the average crystallite size \(< D >\) was found increased and that is from 26 to 23 nm respectively.
Table 1. Crystal structure, lattice cell parameters and phase purity of Ba$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ synthesised by CMHM method.

| Sample Name     | As-prepared | Calcined at 830 [°C] | Sintered at 850 [°C] |
|-----------------|-------------|----------------------|----------------------|
| **Method**      | **Composite Mediated Hydrothermal Method (CMHM)** |
| **Crystal Structure** | Barium Nitrate | Orthorhombic | Orthorhombic | Orthorhombic |
| Phase Purity    | 25 %        | 75 %                 | 100%                 | 100%         |
| Lattice constants [Å] | a=3.893(2), b=11.459(1), c=20.35(3) | a=3.868(1), b=11.393(7), c=20.202(6) | a=3.946(3), b=11.435(5), c=20.363(8) |
| $D_{\text{avg int.}}$ | 19 nm       | 26 nm                | 23 nm                |

Table 2. Crystal structure, lattice cell parameters and phase purity of Ba$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ synthesised by WOWS sol-gel method.

| Sample Name | As-prepared | Calcined at 830 [°C] | Sintered 850 [°C] |
|-------------|-------------|----------------------|-------------------|
| **Method**  | **WOWS Sol-gel Method** |
| **Crystal Structure** | Orthorhombic | Orthorhombic | Orthorhombic |
| Phase Purity | 100 %       | 100 %               | 100 %             |
| Lattice constants [Å] | a=3.879(2), b=11.479(9), c=20.35(1) | a=3.854(5), b=11.49(4), c=20.20(1) | a=3.871(3), b=11.44(1), c=20.25(1) |
| $D_{\text{avg int.}}$ | 27 nm       | 41 nm                | 26 nm              |

In WOWS sol-gel method phase pure orthorhombic crystal structure (JCPD card no. 01-083-0377) was confirmed. After heat treatment (calcination, sintering), crystallite size, lattice parameters, and cell volume were also changed as shown in Table 2. After calcination and sintering of the samples, the average crystallite size $<D>$ was found increased and that is from 41 to 26 nm respectively.

Table 3. Crystal structure, lattice cell parameters and phase purity of Ba$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ synthesised by Co-Precipitation method.

| Sample Name | As-prepared | Calcined at 830 [°C] | Sintered 850 [°C] |
|-------------|-------------|----------------------|-------------------|
| **Method**  | **Co-precipitation Method** |
| **Crystal Structure** | Monoclinic | Orthorhombic | Orthorhombic |
| Phase Purity | 100%        | 100%                | 100%              |
| Lattice constants [Å] | a=4.995(3), b=5.59(2), c=9.2070(4) | a=3.93(2), b=11.39(1), c=20.22(7) | a=3.8126(1), b=11.444(7), c=20.2265(4) |
| $D_{\text{avg int.}}$ | 26 nm       | 28 nm                | 25 nm              |
In Co-precipitation method, monoclinic phase was appeared in as-prepared sample whereas phase pure orthorhombic crystal structure (JCPD card no. 01-083-0377) formed after calcination at 830 °C. After heat treatment (calcination, sintering), crystallite size, lattice parameters, and cell volume were also changed as shown in Table 3. After calcination and sintering of the samples, the average crystallite size < D > was found increased and that is from 28 to 25 nm respectively.

Electrical Properties

**DC Electrical Properties.** DC conductivity (Eq. 2) with respect to temperature ranging from 100 to 500°C was calculated using the formula:

\[
\sigma = \frac{L}{RA}
\]  

(2)

Where A is the area of the pellet and L is the thickness of the pellet.

DC conductivities of the samples synthesized by different three methods as shown in the Fig. 4. DC conductivities increased with increase in temperature for all the samples synthesized by the three different methods. The magnitudes of observed DC electrical conductivities were 0.03Scm⁻¹, 0.01 Scm⁻¹ and 0.04 Scm⁻¹ at 500 °C for CMHM, WOSS sol-gel and co-precipitation method respectively. The CMHM and co-precipitation method show better values of conductivity than WOSS sol-gel method as shown by fig.4. The increase in conductivity is very sharp after 400 °C in case of CMHM and co-precipitation method whereas after 450 °C in case of WOSS sol-gel method. The conductivity mechanism is linked to polaron hopping. With the sufficient thermal energy provided, electrons cross the barrier and take part in hopping. With the increase in temperature, rate of successful hopping increases that in turns increases the conductivity [4,13]. The increase in temperature increases the vacancy sites which are also responsible for increase of conductivity following jump relaxation model [14].

**AC Electrical Properties.** The AC electrical properties of the pellets were calculated with the help of two probes method with the contacts on both pellets faces. The impedance of synthesized samples was calculated as a function of temperature (100-600 °C) at fixed frequency of 10kHz on Wayne Kerr LCR meter 6440B. When applying an AC field, the impedance is the ratio between applied voltage and current. Because of the phase difference among these magnitudes, impedance is a complex function of frequency (\(\omega=2\pi f\)).

\[
Z(\omega)=Z'(\omega)+iZ''(\omega)
\]  

(3)

Fig. 3. DC conductivity vs temperature of Ba_{0.5}Sr_{0.5}CoO_{3-δ} for the temperature range of (100-600 °C).
Where \( Z \) is the total impedance. \( \omega \) is the angular frequency in rad/s, and \( f \) is AC electric field frequency.

![Graph](image)

Fig. 4. Impedance \( (Z) \) vs temperature of \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta} \) in the temperature range of (100-600 °C).

Impedance decreased with increase in temperature in samples synthesized by all methods. At lower temperatures, the higher value of total impedance \( (Z) \) in samples (figure 4) is due to presence of all polarizations that is space charge, dipole, electronic and ionic polarizations [2]. As the temperature is increased, the rate of successful hopping increases so conductivity increases and as a result impedance was decreases. At higher temperature, sufficient thermal energy was available for the electrons to hop. With increase in rate of successful hopping, conductivity increases and hence impedances decrease [2,13].

Conclusions

Barium strontium cobaltite phase pure nano particles were successfully synthesized by wet chemical methods. XRD analysis confirmed the monoclinic crystal structure for as prepared sample synthesized by co-precipitation method whereas orthorhombic phase was appeared in samples synthesized by WOWS sol-gel and CMHM method. After heat treatment, the orthorhombic phase was confirmed in samples synthesized by all three wet chemical methods. The average crystallite size of sintered samples was 23 nm, 26 nm and 25nm, synthesized by CMHM, WOWS sol-gel method and co-precipitation method respectively. For hydrothermally synthesized sample, the observed decreases in impedance was from 6.413 kΩ to 2.09 Ω with increased in temperature (100 - 600 °C). On the other hand, decrease in impedance was observed that is 3.608 kΩ to 7.80 Ω and 97.942 kΩ to 2.05 Ω for samples synthesized by sol gel method and co-precipitation method respectively. The DC electrical conductivities were found as 0.03Scm\(^{-1}\), 0.01 S cm\(^{-1}\) and 0.04 S cm\(^{-1}\) at 500°C for CMHM, WOWS sol-gel and co-precipitation method respectively. The CMHM and co-precipitation method shows better values of conductivity than WOWS sol-gel method.

The prominent decrease in impedance and increase in dc conductivity for hydrothermally synthesized samples shows that CMHM method is best method to synthesize this material and consequently strontium cobaltite can be a potential candidate as an electrode material for intermediate temperature range solid oxide fuel cell (IT-SOFC).
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