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Reduced impedance in dual substituted strontium cobaltite nanoparticles for renewable energy applications

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Abstract

$\text{Sr}_{1-x}\text{Ba}_x\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ (BSCF) nanoparticles were successfully synthesized with three modified wet chemical techniques; composite mediated hydrothermal method (CMHM), without water and surfactants (WOWS) sol-gel and co-precipitation methods. The probable electrical conduction mechanism of synthesized BSCF was explored via complex impedance analysis. Various physico-chemical characterization techniques were employed to study the dependence of structure, homogeneity, physical parameters and electrical properties of BSCF on synthesis procedures. X-ray Diffraction (XRD) confirmed the formation of cubic BSCF perovskite structure. Fourier Transform Infrared Spectroscopy (FTIR) spectra indicated the presence of the fingerprint region of perovskite ($\text{ABO}_3\delta$) structure. Scanning Electron Microscopy (SEM) images revealed uniformly diffused, micro porous and agglomerated morphology. Differential Thermal Analysis (DTA) and Thermogravimetry (TGA) verified the formation of intermediate metal carbonates that were decomposed to the final product. Nyquist plots against frequency (20 Hz–3 MHz) revealed single semi-circular arcs. The arc showed significant grain boundary contribution to total electrical conduction behaviour of BSCF material synthesized by CMHM and co-precipitation methods. Modulus analysis showed the Debye type conductivity relaxation in CMHM synthesized material. The AC conductivity graphs followed Jonscher’s power law. Temperature dependent (RT to 600 °C; 10 kHz) impedances showed decreasing trend that was an indication of thermally activated conduction process. A Correlation was established among structural and electrical conduction properties. Hydrothermally synthesized BSCF samples exhibited minimum impedances and maximum AC conductivity, which makes them a potential candidate for cathode material in (IT-SOFCs) applications.

1. Introduction

Renewable energy pathways have gained worldwide importance as an energy generation alternative in the future because of inadequate reserves and adverse ecological effects of fossil fuel [1]. Renewable energy pathways also have a significant impact on green economy [2, 3]. Among various renewable energy pathways used for sustainable development, fuel cells gained worldwide interest due to their huge capacity for power generation applications [3]. Fuel cells also fulfill our growing need for sustainable energy resources along with significant environmental advantages [4]. Among all fuel cell types, solid oxide fuel cells at intermediate temperature (IT-SOFCs) making an impact in the energy area because of the benefits over other fuel cells. These benefits include fuel flexibility, high efficiency, and low emissions [5, 6]. In IT-SOFCs, particularly cathode material should meet some critical requirements, like high oxygen and electronic transport properties [7]. To fulfill these requirements, two main approaches have been adopted, searching for novel chemical compositions [8] and developing new synthesis routes [9] or improving the current synthesis and processing procedures [10]. Perovskites ($\text{ABO}_3\delta$) based materials containing alkaline-earth and cobaltite have mixed electronic and ionic conductivity (MIEC). These materials can serve as cathodes for IT-SOFCs [11, 12]. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
(BSCF) is a good example of perovskite-based compound. This compound has gained interest among researchers as an effective cathode material in IT-SOFCs applications due to its excellent characteristics for intermediate temperature \([5, 11–14]\). However, industrial applicability of BSCF is still so far limited due to its chemical instability \([15, 16]\) and reactivity towards carbon dioxide gas \([17]\). Nonetheless, BSCF is still an admirable material due to its high conductivity, catalytic activity and outstanding oxygen transport properties which make it excellent cathode material in IT-SOFCs applications \([13, 14, 18–20]\). \(\text{Ba}_0.5\text{Sr}_0.5\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}\) (BSCF) was the best reported composition so far, synthesized by sol-gel technique. In the literature, different routes have been adopted so far to synthesize BSCF cathode material such as solid-state reaction route \([13, 14, 21–23]\), EDTA complexing method \([22, 24, 25]\) etc. Besides these synthesis methods, wet chemical methods have good control on complex composition synthesis and good chemical homogeneity of the final product \([26–31]\). Therefore, in this work modified and easy to handle wet chemical synthesis techniques were designed to synthesize BSCF as promising IT-SOFCs cathode material. The techniques include, composite mediated hydrothermal method (CMHM), WOWS sol-gel and co-precipitation methods. Physicochemical characterizations of the synthesized BSCF nanoparticles were done to confirm the feasibility of the wet chemical synthesis techniques. The current work was intended to explore the relationship among modified synthesis recipes, processing parameters, microstructures and their effects on structural and electrical conduction behaviour of BSCF material. In addition, among numerous studies in the literature impedances was investigated with respect to change of frequencies at different temperatures. However, in the present work, we investigated and compared probable electrical conduction behaviour via complex impedance analysis i.e. Nyquist plots, Modulus plots, dielectric studies and AC conductivity against frequency at room temperature. Moreover, impedances were also measured and compared against temperature (RT-600 °C) at a fixed frequency (10 kHz). Such comparative studies of these modified synthesis techniques for BSCF and its probable electrical conduction behaviour via complex impedance analysis have not been reported so far in the literature, to the best of our knowledge.

2. Experimental

2.1. Materials and methods

Composite mediated hydrothermal method (CMHM), WOWS sol-gel and co-precipitation methods were the three different modified wet chemical approaches employed to prepare BSCF nanoparticles. Barium nitrate \(\text{Ba(NO}_3\text{)}_2\) (Fisher Scientific), strontium nitrate \(\text{Sr(NO}_3\text{)}_2\) (Sigma-Aldrich), iron nitrate nonahydrate \(\text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}\) and cobalt nitrate hexahydrate \(\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\) (Panreac Quimica Sau) were used as precursors.

2.2. Synthesis

2.2.1. Composite mediated hydrothermal method (CMHM)

BSCF nanoparticles were synthesized through CMHM by utilizing sodium hydroxide (NaOH) and potassium hydroxide (KOH) (Sigma-Aldrich) as reactant and precipitating agents. Molar ratio \((0.515:0.485)\) was used for the NaOH-KOH as a reactant and precipitating process. Eutectic point of this system was 170 °C \([30–33]\). Firstly, precursors were well ground, mixed and put in a Teflon container. Later it was placed in a pre-heated oven set at a temperature of 180 °C for a time limit of 65 min \([30, 31, 33]\). After 65 min, the oven was switched off and allowed to cool at room temperature. The contents of the vessel were washed many times by deionized water to eliminate nitrates and other impurities. Washed sample was dried at 105 °C in an electric oven.

2.2.2. WOWS sol-gel method

BSCF nanoparticles were prepared by sol-gel method. Precursors were dissolved in ethylene glycol having a ratio \((1:14)\) with parallel constant stirring at room temperature. When homogenous solution was formed, the temperature increased up to 80 °C for 2 h. Upon the formation of gel, the temperature was further increased up to 200 °C. Finally, the formed gel was burnt up to fine powder.

2.2.3. Co-precipitation method

In co-precipitation method, synthesis was done by preparing 0.4 M solutions of all precursors in deionized water. 2 M Sodium Hydroxide (NaOH) solution in deionized water was used as a precipitation agent. All solutions were mixed with continuous stirring to a homogenous solution. Co-precipitation agent was added and mixed to all the precursor solutions at room temperature. When homogenous solution was formed, the temperature increased up to 70 °C. Precipitated particle sizes were controlled by monitoring the co- precipitation steps and maintaining the pH of 8.5. Finally, the synthesized precipitates were washed and dried. In all the above methods; obtained powders were calcined at 830 °C for 120 min. Calcined powders were converted into pellets and were sintered at 850 °C for 20 min for further characterizations.
3. Characterizations

3.1. X-ray diffraction
Diffraction pattern of the material was studied by using Pan Analytical Xpert Pro diffractometer. The scanning of samples in 2θ range (20°–80°) was done by Cu Kα radiation source. Scherer formula (equation (1)) was used to calculate the average crystallite sizes \( D \) of the synthesized samples:

\[
D = \frac{k \lambda}{\beta \cos \theta}
\]

Where \( k \) in equation (1) is called the shape constant having a magnitude of 0.9, \( \lambda = 1.54 \text{ Å} \) in the equation is the x-ray source wavelength, \( \beta \) in the equation is the full width at half maximum (FWHM) and \( \theta \) in the equation is the Bragg’s angle.

3.2. Scanning electron microscopy (SEM)
Surface morphology of the synthesized BSCF material was studied by using SEM (JSM.6610LV, JEOL, Japan) equipped along with energy dispersive x-ray spectroscopy (EDX).

3.3. Fourier transform infrared spectroscopy (FTIR)
Fourier Transform Infrared Spectrophotometer (IRTracer-100; Shimadzu Japan) equipped with an ATR system (Quest Single Reflection ATR Diamond GS10800 Specac, UK) was used for the FTIR analysis of the synthesized BSCF samples. The selected range was 400–4000 cm\(^{-1}\) in the Mid-infrared spectrum with a resolution of 4 cm\(^{-1}\) and 80 scans per sample were recorded. Software Spectrum (Lab solutions version 1.81 (Shimadzu Japan Instrument) was applied to process the spectra.

3.4. Thermal analysis (DTA/TGA)
Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were simultaneously performed by using the instrument (DTG-60; Shimadzu Japan). All samples were scanned from room temperature to 1200 °C at a heating rate of 5 °C min\(^{-1}\) using an empty Al\(_2\)O\(_3\) crucible as reference.

3.5. Electrical properties
3.5.1. AC characteristics of perovskite Ba\(_{0.5}\)Sr\(_{0.5}\)Co\(_{0.8}\)Fe\(_{0.2}\)O\(_3\) nanoparticles
Wayne Kerr LCR meter 6440B was utilized for the impedance (\( Z \)) measurement of the synthesized samples in the frequency range (20 Hz to 3 MHz) at room temperature. Moreover, impedances (\( Z \)) were also measured and compared in the temperature range (RT to 600 °C) at a fixed frequency (10 kHz). AC electrical properties of the pellets were calculated by the two-probe method. Impedance is a complex function of frequency:

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

Where (\( Z \)) is the total impedance. (\( Z' \)) and (\( Z'' \)) are the real and imaginary parts of impedance.

4. Results and discussion

4.1. Structural analysis (x-ray diffraction)
Figure 1 shows the indexed XRD patterns for the BSCF samples calcined at 830 °C, synthesized by CMHM, WOWS sol-gel and co-precipitation methods respectively. Hydrothermally synthesized samples displayed 34% BSCF cubic phase (JCPD card no. 00-055-0563, space group Pm-3m 221) along with 24% BSCF Hexagonal phase, 12% BSC hexagonal phase (JCPD card no. 00-052-1613, space group P6\(_3\) mmc, 194), 14% barium nitrate raw material peak (JCPD card no. 00-024-0053) and 16% strontium nitrate raw material peak (JCPD card no. 00-048-0599). XRD diffraction patterns for samples synthesized via WOWS sol-gel method displayed 92% BSCF cubic phase (JCPD card no. 00-055-0563, space group Pm-3m 221) along with 8% raw material barium nitrate peak (JCPD card no. 00-024-0053). XRD diffraction patterns for samples synthesized via co-precipitation method displayed 84% BSCF cubic phase (JCPD card no. 00-055-0563, space group Pm-3m 221) along with 16% BSC hexagonal phase. Average crystallite sizes calculated for the cubic phase using the Scherrer formula were 29 nm, 13 nm and 16 nm for the samples produced with CMHM, WOWS sol-gel and co-precipitation techniques respectively.

4.2. Scanning electron microscopy (SEM)
SEM was used to study the microstructures of the material. Morphology of BSCF calcined samples, synthesized by CMHM, WOWS sol-gel and co-precipitation methods were shown in figures 2(a)–(e)–4(a)–(e) respectively. As evident from the SEM images, the synthesis methods significantly affect the morphology. In all cases it seems...
that, calcined powder samples are forming clusters. The clusters were formed because of nanoparticles agglomeration. In case of the particles synthesized with CMHM method; diffused, micro porous, agglomerated, flower like clustering of the nano particles was observed, as evident from figures 2(a)–(e). Small particles were embedded on the surface of clustered surfaces as showed in figure 2(e). The samples prepared by CMHM technique displayed fine powder, more uniform grain size distribution, good connectivity among grains and homogenous microstructure suggesting a good electrical conductivity [10, 34–37]. The clusters were formed because of particles agglomeration which was widely seen throughout the sample. Small spherical particles were embedded on the surface of clustered surfaces as showed in figure 3(e). Figures 4(a)–(e) depicts the amorphous like morphology for the samples synthesized through co-precipitation method. Magnified SEM images show that the connected particles are homogeneous with the presence of porous spherical particles [29]. Small threads are distributed throughout the sample as showed in figures 4(a)–(d). The best performance was observed for the hydrothermally synthesized BSCF material. This was due to the fine microstructure as illustrated in the SEM micrographs (figures 2(a)–(e)) as compared to SEM micrographs obtained from WOWS sol-gel and co-precipitation methods. Moreover, SEM images showed that particles formed via these two techniques have different sizes with non-uniform distribution of particles. The
micrographs for samples synthesized through WOWS sol-gel and co-precipitation techniques showed that tiny particles coalesced to form larger aggregates. This represented a high level of porosity and hence lesser conductivity.

Energy-dispersive x-ray spectroscopy (EDX) study was conducted for the BSCF samples synthesized by wet chemical methods at different sites. EDX spectra is shown in figures 2(f)–4(f) for the samples synthesized with CMHM, WOWS sol-gel and co-precipitation techniques respectively. The best compositional homogeneity was attained for CMHM synthesized samples as showed in figures 2(a)–(f). SEM study confirmed that CMHM method is suitable method for the synthesis of highly homogeneous BSCF perovskite materials. Although, it required a careful selection of reaction parameters.

4.3. Fourier transform infrared spectroscopy (FTIR)

FTIR spectrums of nanocrystalline BSCF samples synthesized by CMHM, WOWS sol-gel and co-precipitation techniques is shown in figures 5(a)–(c) respectively. In the FTIR spectra, four distinct absorption peaks were observed about 400-550, 746, 858 and 1450 cm$^{-1}$ [10, 34–37]. Absorption bands found near 746 cm$^{-1}$ were due
to the existence of metal oxygen bond in the perovskite structure [10]. Some recent studies have shown that the nitrates of precursors compounds may decompose into their corresponding oxides [10, 34–37]. The absorption bands appearing at 858 cm$^{-1}$ and near 1450 cm$^{-1}$ indicate the presence of twisting and stretching vibration of carbonate CO$_3^{2-}$ in the samples [10, 34–37]. FTIR spectra also showed absorption peaks in the range of 400–550 which are recognised as BO$_6$ octahedron of stretching and bending vibrations of metal cations [34]. Moreover, FTIR results showed that, this technique is more efficient as compared to XRD in detection of carbonates present in the samples.

4.4. Thermal analysis (DTA/TGA)

TGA and DTA techniques are widely used to investigate the decomposition mechanism and to obtain evidence concerning the formation of the final product. Figure 6(a) show the TGA-DTA curves for as prepared samples synthesized via CMHM method. The weight of BSCF samples was decreased gradually with the rise in temperature as displayed in figure 6(a). Initial weight loss was observed at 64 °C owing to evaporation of adsorbed water molecules [28, 29, 34, 38, 39]. The endothermic peak centred at 349 °C followed by a second weight loss which was assigned to the formation of oxycarbonates [28]. An endothermic peak centred at 927 °C in the DTA curve. Along with this endothermic change, TGA curve showed a steady weight loss. That weight loss was mainly due to the conversion of oxycarbonates into carbonates, decomposition of impurities (BaCo$_3$, SrCO$_3$) and formation of BSCF (Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$) [28, 29, 34, 38, 40] product. Afterwards, with continues heating up to 1200 °C, led to a slight increase in weight was appeared which was credited to the rise of oxygen content (\(\delta\)) per formula unit cell in Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ [29]. DTA-TGA observations explained above were in good agreement with the FTIR findings of the synthesized product. Figure 6(b) shows that the TGA-DTA curves of the as prepared samples synthesized via WOWS sol-gel method. The weight of BSCF samples was decreased gradually with rise in temperature. An exothermic peak centred at 368 °C was assigned to the burnout of organic matter followed by an initial weight loss [29]. Small endothermic peaks centred at (565 °C, 792 °C) were assigned to the formation of oxycarbonates and decomposition of oxycarbonates to carbonates (BaCO$_3$, SrCO$_3$) along with the evolution of carbon dioxide [28]. After 792 °C, an endothermic peak

Figure 5. FTIR spectra of BSCF as-prepared powdered samples synthesized by (a) CMHM, (b) WOWS sol-gel and (c) co-precipitation methods.
was appeared at 919 °C in the DTA curve. Along with this endothermic change, TGA curve followed a steady weight loss which was assigned to the decomposition of carbonate \((\text{BaCO}_3, \text{SrCO}_3)\) impurities and development of barium strontium iron cobaltite \((\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 - \delta)\) product. Afterwards, with continues heating up to 1200 °C, led to a slight increase in weight was appeared which was credited to the rise of oxygen content \((\delta)\) per formula unit cell in \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 - \delta\) [28, 29, 34, 38, 41].

Figure 6(c) shows the TGA-DTA curves for as prepared samples synthesized via co-precipitation method. The weight of BSCF samples was decreased gradually with rise in temperature. A small endothermic peak centred at 362 °C followed by an initial weight loss which was assigned to the formation of oxycarbonates [28]. After 362 °C, an endothermic peak was appeared at 894 °C in the DTA curve. Along with this endothermic change, TGA curves followed a steady weight loss which was assigned to conversion of oxycarbonates into carbonates, decomposition of carbonates impurities \((\text{BaCo}_3, \text{SrCO}_3)\) and formation of barium strontium iron cobaltite \((\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 - \delta)\) [28, 29, 34, 38, 41] product. Afterwards, with continues heating up to 1200 °C, led to a slight increase in weight was appeared which was credited to the rise of oxygen content \((\delta)\) per formula unit cell in \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 - \delta\) [29].

4.5. Electrical properties

4.5.1. AC characteristics of perovskite \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 - \delta\) nanoparticles

AC electrical behaviour of the strontium cobaltite samples were calculated using two probe method. The complex impedances of the samples were evaluated from \((20\text{ Hz} - 3\text{ MHz})\) at room temperature. Figures 7(a)–(c) depicts the changes in \(Z'\) with frequency for BSCF sample synthesized via three different methods. Hydrothermally synthesized samples attained lowered values of impedance as compared to the samples synthesized by WOWS sol-gel and co-precipitation methods. Figures 7(a)–(c) shows that \(Z'\) was stable up to 100 kHz for CMHM, 10 kHz for WOWS sol-gel and 150 kHz for co-precipitation method. Above these frequencies, value of \(Z'\) was decreased with increase in frequency. That decrease in \(Z'\) was responsible for the increase of AC conductivity due to the release of space charges at higher frequencies [42, 43].

For good understanding of the impedance characteristics and conduction mechanism of the material synthesized by three methods, we analysed cole-cole or Nyquist plots \((Z'\text{ versus } Z'')\) as shown in figures 8(a)–(c). Impedance spectrum in figures 8(a)–(c) showed single semi-circular arcs for all BSCF samples. The presence of
single semi-circular arcs in the impedance spectra was an indication of single-phase contribution of the material in the electrical conduction behaviour. At higher frequency side, the semi-circular arcs were linked to the bulk properties of the material. Whereas at lower frequency side semi-circular arc was related to the interface or grain boundary effects. Zview software was used to fit the experimental results with fitting error <5%. Insets of figures 8(a)–(c) show the equivalent circuits that were used to fit the experimental results. During the fitting of the experimental results, no specific parameter was kept constant. The equivalent circuits used for fitting of the experimental results were comprised on single RC circuit. Here, RC circuit characterized the interface of the synthesized samples. During the fitting of the experimental data, the constant phase element (CPE) was employed in the equivalent circuit for samples synthesized via WOWS sol-gel and co-precipitation methods. The purpose of CPE in the equivalent circuit was to balance the non-ideal capacitive behaviour of the material. Cause of this non-ideal capacitive behaviour was inhomogeneous boundaries or interfaces of the material. The value of capacitance \( C \) was calculated by the formula [43, 44],

\[
C = R^{1-n}Q^{1/n}
\]

(3)

Where \( n \) in the formula was called empirical constant. Magnitude of \( n \) stands for deviation from ideal Debye behaviour. For pure capacitor, the magnitude of \( n \) was unity and for pure resistor the magnitude of \( n \) was zero. On the other hand, to fit the experimental results for samples synthesized via CMHM method two RC circuits along with a resistor \( R_3 \) were used. Scattered symbols in figures 8(a)–(c) identified by the experimental data. Whereas solid lines were indicated by the fitted results found from the circuit used for fitting of experimental data. Results of all samples showed the presence of one relaxation in the material. The parameters found from fitting of the experimental results are shown in table 1 at room temperature. Capacitance values for perovskite BSCF nanoparticles synthesized by CMHM and co-precipitation method were measured and found in the range of \( 10^{-11} \)–\( 10^{-8} \).
the conduction mechanism of perovskite BSCF nanoparticles. On the other hand, capacitance values were found in the range of $10^{-12}$ for the samples synthesized by WOWS sol-gel technique. This capacitance value proposed the presence of bulk effect in the conduction properties of the material [45]. The fitted results agreed well with the experimental impedance data.

Electric modulus is a very useful parameter to describe the relaxation processes in the materials. Therefore, relaxation mechanism of the perovskite BSCF was investigated using the complex electrical modulus spectrum ($M'$ versus $M''$). Figures 9(a)–(c) shows the real and imaginary part of modulus ($M'$ versus $M''$) against frequency for samples synthesized via all methods. Complex electric modulus was described as [46]

$$M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = M' + jM'' = j\omega C_0 Z^*$$  \hspace{1cm} (4)

Here modulus real part ($M'$) is equal to

$$M' = j\omega C_0 Z''$$  \hspace{1cm} (5)

and modulus imaginary part ($M''$) is equal to

$$M'' = j\omega C_0 Z'$$  \hspace{1cm} (6)

| Method         | $R_1$  | CPE     | $n$  | $C$       | $C_1$     | $C_2$     | $R_2$  | $R_3$  |
|----------------|--------|---------|------|-----------|-----------|-----------|--------|--------|
| CMHM           | 639.9  | —       | —    | —         | 1.321E-9  | 8.578E-11 | 214.6  | 290.2  |
| WOWS Sol-gel   | 19385  | 2.401E-9| 0.633| 7.39E-12  | —         | —         | —      | —      |
| Co-precipitation| 4088   | 3.716E-10| 0.858| 4.04E-11  | —         | —         | —      | —      |

Figure 8. Cole-Cole/Nyquist plots between $Z'$ and $Z''$ for the perovskite SrCoO$_{3-\delta}$ samples measured at room temperature with equivalent circuits synthesized by (a) CMHM, (b) WOWS sol-gel and (c) co-precipitation methods.
Single semi-circular arcs were obtained for BSCF samples as showed in figures 9(a)–(c). The single arcs indicated the presence of single dominant relaxation phenomena in the material and hence supported the impedance results. To further understand the relaxation behaviour, the joint variation of $M''$ and $Z''$ with respect to frequency was studied. Figures 10(a)–(c) depicts the variation of $M''$ and $Z''$ for perovskite BSCF samples synthesized via all methods. At higher frequencies, the appearance of a single peak in the $M''$ versus $Z''$ graphs pointed to the presence of only one frequency dependent dielectric relaxation process in perovskite BSCF samples [43, 47]. Figures 10(a) and (b) showed that the value of $Z''$ increased at higher frequencies for hydrothermally and sol-gel synthesized samples. But, the value of $Z''$ decreased at higher frequencies (above 100 kHz) for co-precipitation synthesized samples as showed in figure 10(c). This decrease in $Z''$ indicated the release of space charges in the material [43]. Curves of $M'$ and $Z'$ almost overlapped each other on higher frequencies in the case of co-precipitation synthesized samples. Generally, overlapped peak position points towards some specific conduction mechanism. Mechanisms involved are either delocalized or long-range conduction [46]. On the other hand, non-overlapping behaviour of $Z''$ and $M''$ indicated that the material had components from both localized and long-range relaxation as displayed for CMHM and sol-gel synthesized samples. Modulus analysis also expressed support for the impedance analysis of the existence of only one frequency dependent dielectric relaxation process. In addition, modulus analysis confirmed the Debye type conductivity relaxation in the hydrothermally synthesized samples.

Variation in AC conductivity against frequency is shown in figures 11(a)–(c) for the perovskite BSCF samples. Hydrothermally synthesized samples attained higher values of AC conductivity as compared to samples synthesized by other methods. Two regions were clearly observed in the conductivity plots. The frequency independent region (at low frequencies) was generally mentioned as dc part of the conductivity. DC part of the conductivity ($\sigma_{dc}$) was calculated from fitting of AC conductivity ($\sigma_{ac}$) curves. Whereas, the frequency dependent region (at higher frequencies) was generally mentioned as AC part of the conductivity. In the frequency dependent region, conductivity increased with the increase in frequency. This behaviour indicated that the conductivity plots follow Jonscher's power law [48].

Figure 9. Modulus plane plots for the perovskite SrCoO$_{3-\delta}$ samples measured at room temperature synthesized by (a) CMHM, (b) WOWS sol-gel and (c) co-precipitation methods.
Where $\sigma_{ac}$ is frequency independent part of the conductivity (dc part at lower frequencies). $A$ and $s$ in equation (7) are the temperature dependent constants. The slope of $s$ changes at a particular frequency. That frequency is referred to as the hopping frequency. Conductivity depends on the hopping of charge carriers. The conductivity was increased due to increase of hopping of charge carriers as the frequency of applied field increases. Usually, long range drive of mobile charge carriers was dominated at higher frequencies. Dielectric permittivity ($\varepsilon'$) and dielectric loss tangent ($\tan \delta$) against frequency for hydrothermally synthesized perovskite BSCF samples were also in good agreement with the impedance and AC conductivity results. Both characteristics were discussed in the supporting information section is available online at stacks.iop.org/MRX/7/015525/mmedia.

Variation in the impedance of BSCF samples synthesized via wet chemical method were also evaluated and compared. Figure 12 indicate that the impedance magnitude showed a decreasing trend against temperature (RT - 600 °C) at a fixed frequency of 10 kHz for all BSCF samples. Hydrothermally synthesized samples attained the lowest values of impedance (1.35 Ω at 600 °C) as compared to impedance of the samples synthesized by other methods as showed in table 2. Higher magnitude of total impedances ($Z$) at lower temperatures was credited to the presence of space charge, dipole, electronic and ionic polarizations [27, 33]. With the successive increase of temperature, electrons gained adequate thermal energy required for hopping. The decrease of impedance and increase of conductivity against temperature was due to increase of the rate of successful hopping [27, 33, 41]. Moreover, decrease of impedance can be caused by the increase of vacant sites with the increase of temperature (100 to 600 °C). This phenomenon was utilized to attain the higher values of conductivity as described in the jump relaxation model [49]. In addition, the lower value of impedances in hydrothermally synthesized samples was caused by the largest average crystallite size of the synthesized particles. The larger crystallite size resulted in small grain boundary densities [50, 51]. Therefore, the resistance due to grain boundaries was smaller in CMHM synthesized samples as compared to other methods. As the grain boundaries resistance was reduced, the opposition provided by the electrons to hop decreased. Consequently, impedance of hydrothermally synthesized decreased at higher temperatures [41, 50, 51]. The dominant conduction mechanism in this case was conduction along the and through the grain boundaries [40]. Moreover, ionic hopping in these
Figure 11. Frequency dependence of AC conductivity measured at room temperature for perovskite $\text{SrCoO}_{3-\delta}$ samples synthesized by (a) CMHM, (b) WLOS sol-gel and (c) co-precipitation methods.

Figure 12. Impedance (Log $Z$) versus temperature (RT-600 °C) of BSCF samples at fixed frequency of 10 kHz synthesized by CMHM, WLOS sol-gel and co-precipitation methods.
Table 2. Impedances (Z) as a function of temperature (RT–600 °C) at fixed frequency of 10 kHz of BSCF samples synthesized by WOES sol-gel, co-precipitation and CMHM methods.

| Synthesis method                  | Impedance (Z)   |
|-----------------------------------|-----------------|
| CMHM (RT–600 °C)                  | 1093–1.35Ω      |
| WOES sol-gel (RT–600 °C)          | 18213–80.70Ω    |
| Co-precipitation (RT–600 °C)      | 3935–21.57Ω     |

materials can be explained through both Jonscher’s rule and Arrhenius equation [32]. At higher temperatures, lower values of impedance of BSCF samples indicated that the ionic conduction is dominant.

5. Conclusions

The present work reports successful synthesis of nano crystalline BSCF material by three modified wet chemical methods. The electrical conduction behaviour of BSCF was explored via complex impedance plane plots against frequency (20 Hz–3 MHz). XRD, FTIR and DTA-TGA confirmed the formation of perovskite type BSCF material after heat treatment at lower temperatures of 830 °C. SEM micrographs showed that, hydrothermally synthesized sample had fine powder, more uniform grain size distribution, good connectivity among different grains and homogenous microstructure. These morphological features played an important role in enhancing the electrical conduction of hydrothermally synthesized BSCF samples. Nyquist plots of the samples synthesized with hydrothermal and co-precipitation methods revealed the presence of grain boundary phases, whereas bulk phases for samples synthesized with sol-gel method. RC equivalent circuits revealed the electrical conduction parameters and relaxation processes which were associated with grain boundaries and bulk effects. Modulus study showed the presence of one relaxation in all samples and hence supported the impedance results. Modulus analysis confirmed the Debye type conductivity relaxation of hydrothermally synthesized samples. Dielectric properties, loss tangent and AC conductivity were in good agreement with the impedance results. AC conductivity (σac) against frequency followed Jonscher’s power law and hoping model. Temperature dependent (RT to 600 °C; 10 kHz) impedances showed decreasing trend that was an indication of thermally activated conduction process. That conduction process was clarified via polarization phenomena, hopping model and lattice oxygen vacancies. Consequently, hydrothermally synthesized BSCF nanoparticles had the advantages of simplicity, better control, homogeneous microstructure, lowers values of impedance and higher values of AC conductivity as compared to other methods. BSCF compound synthesized via hydrothermal method may be a potential candidate in renewable energy applications especially as an electrode (cathode) material for intermediate temperature range solid oxide fuel cells (IT-SOFCs).

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