



Electrochemical Properties of Ti- And Zr-Doped BSCF Cathodes for Intermediate-Temperature Solid Oxide Fuel Cells

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ABSTRACT

The BSCFTi, Barium Strontium Cobalt Iron Titanate ($\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Ti}_x\text{O}_{3-\delta}$) and BSCFZr, Barium Strontium Cobalt Iron Zirconate ($\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$), where δ represents oxygen deficiency and x represents various dopant compositions, cathode powders were synthesized by the sol-gel method using nitrate-based precursor chemicals for SOFC applications. These materials are highly suitable as cathodes for solid oxide fuel cells because of their enhanced electrochemical and oxygen ion transport properties. To obtain low over potential cathode materials, the sol-gel technique was adopted for the preparation of nano-sized powders. The prepared powders were calcined at 900°C for 8 hours and sintered at 1050°C for 6 hours. The synthesized samples were characterized using X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDAX), and ionic conductivity measurements.

Keywords: SOFC, BSCFTi, BSCFZr, Sol-Gel Method, XRD, SEM/EDAX, TGA/DTA, Ionic Conductivity, Density.

1. INTRODUCTION:

Solid oxide fuel cells (SOFCs) are among the most important electrochemical energy conversion devices because of their high efficiency, fuel flexibility, and environmentally friendly operation. A major advantage of SOFCs is their high concentration of oxygen vacancies, which enhances oxygen ion transport and improves electrochemical performance [1–3]. Among various cathode materials such as LSM, SSC, LSCF, and BSCF, BSCF-based perovskites have attracted significant attention due to their excellent ionic and electronic conductivity, superconductivity, ferro-electric behavior, and high oxygen reduction activity [4–6]. However, the thermo-mechanical compatibility between the electrolyte and cathode, High electronic conductivity, High ionic conductivity, Stability under oxidizing conditions, large triple phase boundary (TPB) area [14,15] remains a major challenge in SOFC operation. Recently developed BSCF cathodes have demonstrated remarkably high power densities of approximately 1010 mW/cm² at 600°C and 402 mW/cm² at 500°C, which are significantly higher than those of conventional cathodes [12]. In these systems, hydrogen is commonly used as fuel while air acts as the oxidant at the cathode. BSCF materials are also suitable for single-chamber SOFC operation due to their high oxygen diffusivity and excellent catalytic activity for oxygen reduction reactions [13]. This limitation can be overcome by introducing suitable dopants or impurities into the cathode structure. The addition of Titanium (Ti) and Zirconium (Zr) separately into the B-site of the ABO₃ perovskite structure of BSCF can improve ionic conductivity and reduce cathodic over potential [7,8]. In these materials, oxygen ion vacancies are generated along the

(Co^{3+/4+}, Fe^{3+/4+})-O₂-(Co^{3+/4+}, Fe^{3+/4+}) pathway because of the overlap between oxygen p-orbitals and transition-metal d-orbitals, thereby enhancing oxygen ion mobility. Furthermore, the presence of Ba²⁺ at the A-site increases the concentration of higher valence B-site ions such as Co⁴⁺ and Fe⁴⁺, which further promotes oxygen vacancy formation and improves conductivity and overall SOFC efficiency [9,10]. The preparation of BSCF cathodes doped with Ti and Zr and the study of their over potential characteristics remain highly important because these dopants facilitate rapid oxygen ion transport. Improved performance can also be achieved by increasing cathode porosity, which enhances gas diffusion and oxygen reduction reactions [18]. Consequently, higher current density can be generated due to improved oxygen transport, faster electrode kinetics, and increased participation of charge carriers in electrochemical reactions. Studies by Itoh et al. and co-workers have shown that the coexistence of covalent and ionic bonding in BSCFO_{3-δ} significantly enhances both electronic and oxygen ion conductivity even at relatively low temperatures. Their studies also revealed that oxygen stoichiometry decreases with increasing temperature, leading to reduction of B-site cations and enhanced oxygen vacancy concentration [19, 20]. The performance of SOFC cathodes strongly depends on several preparation parameters such as reactant purity, stoichiometry, calcination temperature, sintering conditions, and chemical processing routes.

In the present work, cathode materials suitable for single-chamber SOFC operation were prepared by doping small impurities of Ti and Zr into BSCF with increasing concentrations. The investigated compositions include: Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{1-x}Ti_xO_{3-δ} and Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{1-x}Zr_xO_{3-δ} where x = 0, 0.10, 0.15, and 0.20, with δ = 0. These compositions, referred to as BSCFT (1,2,3,4) and BSCFZr (1,2,3,4) respectively, were synthesized and characterized to evaluate their thermal, structural, and electrochemical properties.

2. MATERIALS AND METHODOLOGY:

Commercial analytical reagent (AR) grade chemicals supplied by Sigma-Aldrich were used for the preparation of cathode materials in the present investigation. The chemicals employed included Ethylene Diamine Tetra-Acetic Acid (EDTA), ethylene glycol, acetic acid, ammonia solution, and nitrate salts of Barium, Strontium, Cobalt, and Iron, along with Titanium oxide (TiO₂) and Zirconium oxide (ZrO₂). The synthesized cathode materials belong to the perovskite family of oxides, which are widely recognized for their excellent mixed ionic-electronic conductivity and superior oxygen reduction reaction activity, making them suitable candidates for intermediate-temperature Solid Oxide Fuel Cells (SOFC) applications [2,4,7].

In the present work, nano-crystalline cathode materials of Titanium and Zirconium substituted BSCF were synthesized with the compositions Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{1-x}Ti_xO_{3-δ} (BSCFT) and Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{1-x}Zr_xO_{3-δ} (BSCFZr), where the dopant concentration x was varied as 0, 0.10, 0.15, and 0.20. BSCF-based cathodes are considered highly promising materials for intermediate-temperature SOFCs due to their superior oxygen ion conductivity and excellent catalytic activity toward oxygen reduction reactions [4,12,18]. The substitution of Ti and Zr ions into the BSCF lattice was carried out to improve structural stability, thermal compatibility, oxygen vacancy concentration, and electrochemical performance of the cathode materials. Doping with transition metal ions is known to enhance the electrical conductivity and long-term stability of SOFC cathodes by modifying the crystal structure and reducing thermal expansion mismatch [15,18,21].

The cathode powders were synthesized using the sol-gel technique, which is considered one of the most effective and economical chemical routes for obtaining homogeneous nano-sized ceramic powders with high purity and better compositional control. Compared with conventional solid-state reaction methods, the sol-gel route offers lower calcination temperatures, uniform mixing of cations at the molecular level, fine particle size distribution, and improved sintering characteristics [3,11]. The method also provides excellent control over stoichiometry and phase purity, which are essential for obtaining highly crystalline perovskite structures suitable for SOFC applications [1,20].

The precursor chemicals used for synthesis were Barium nitrate [$\text{Ba}(\text{NO}_3)_2$], Strontium nitrate [$\text{Sr}(\text{NO}_3)_2$], Cobalt nitrate [$\text{Co}(\text{NO}_3)_2$], Iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], Titanium oxide (TiO_2), and Zirconium oxide (ZrO_2). Stoichiometric quantities of the precursor materials were accurately weighed according to the required compositions using a digital analytical balance. The molar ratio of Ba: Sr was maintained at 0.5:0.5, while the Co: Fe ratio was fixed at 0.8:0.2 throughout the synthesis process. The precursor powders were dissolved separately in distilled water under continuous stirring to obtain homogeneous solutions. Acetic acid was added as a complexing agent to enhance dissolution and maintain solution stability, while ammonia solution was used to adjust the pH and facilitate the chelation process. The cation-to-nitrate (C/N) ratio was maintained at 0.5 to ensure proper gel formation and homogeneous distribution of metal ions throughout the solution [11,20].

EDTA and ethylene glycol played an important role during synthesis. EDTA acted as a chelating agent by forming stable complexes with metal ions, thereby preventing premature precipitation and ensuring uniform cation distribution. Ethylene glycol functioned as a polymerizing agent and promoted the formation of a three-dimensional polymeric network during gel formation. The combination of EDTA and ethylene glycol in the sol-gel process is known to produce highly homogeneous nano-structured powders with reduced agglomeration and improved particle dispersion [3,20].

The prepared solution was transferred into a borosilicate glass beaker and continuously stirred using a magnetic stirrer equipped with a hot plate for approximately 4 hours to obtain a homogeneous mixture. During stirring, the temperature was gradually increased between 80°C and 100°C to facilitate solvent evaporation and initiate gel formation. Continuous heating transformed the solution into a viscous gel due to polymerization and solvent removal. After gel formation, the stirring speed was reduced and heating was continued until self-combustion occurred, producing a fluffy ash-like precursor powder. The self-combustion process released gases such as CO_2 , NO_2 , and H_2O vapor, resulting in porous nano-sized precursor powders [11].

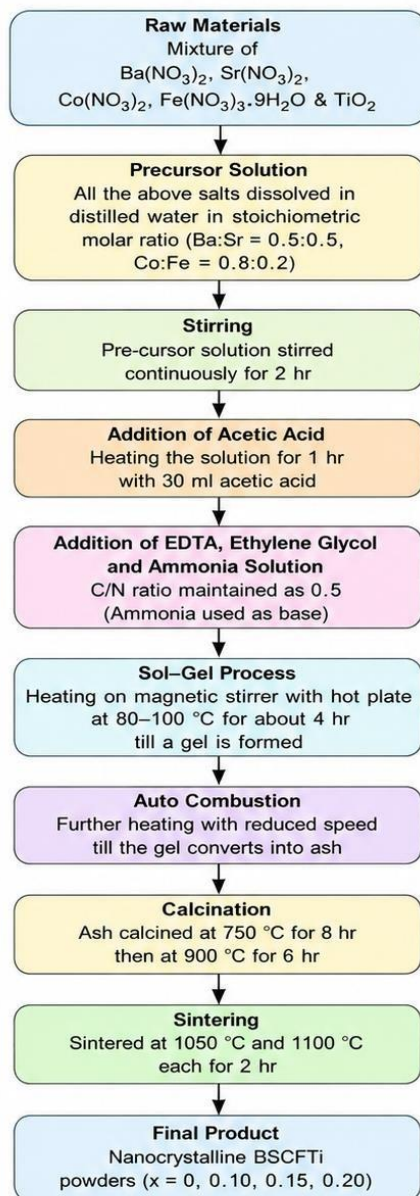
The obtained ash was initially calcined at 800°C for 8 hours to remove residual organic compounds and intermediate phases. Further calcination was carried out at 900°C for 6 hours to promote crystallization and formation of the single-phase perovskite structure. Finally, the powders were sintered at 1050°C and 1100°C for 2 hours each to improve grain growth, crystallinity, and phase stability of the synthesized cathode materials. High-temperature sintering is essential for achieving dense and well-crystallized perovskite phases suitable for electrochemical applications [2,11,18].

The synthesized BSCFT and BSCFZr powders were characterized using various analytical techniques to evaluate their structural, morphological, thermal, optical, vibrational, and electrical properties. X-ray diffraction (XRD) analysis was carried out to determine phase formation, crystallite size, lattice parameters, and crystal structure of the synthesized materials. Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Analysis (EDAX) was used to study surface morphology, grain distribution, porosity, and elemental composition of the samples. Thermo Gravimetric and Differential Thermal Analysis (TGA/DTA) were employed to investigate thermal decomposition behaviour, weight loss characteristics, and phase transformation temperatures during calcination. Fourier Transform Infrared Spectroscopy (FTIR) was utilized to identify metal-oxygen bonding and functional groups present in the materials. UV-Visible spectroscopy was used to estimate optical absorption characteristics and optical band gap energy, while Raman spectroscopy provided information regarding lattice vibrations and structural distortions within the perovskite lattice [5,19]. Electrochemical impedance spectroscopy was performed to study electrical conductivity, polarization resistance, and charge transport behavior of the synthesized cathodes for SOFC applications [7,16,17,22,23].

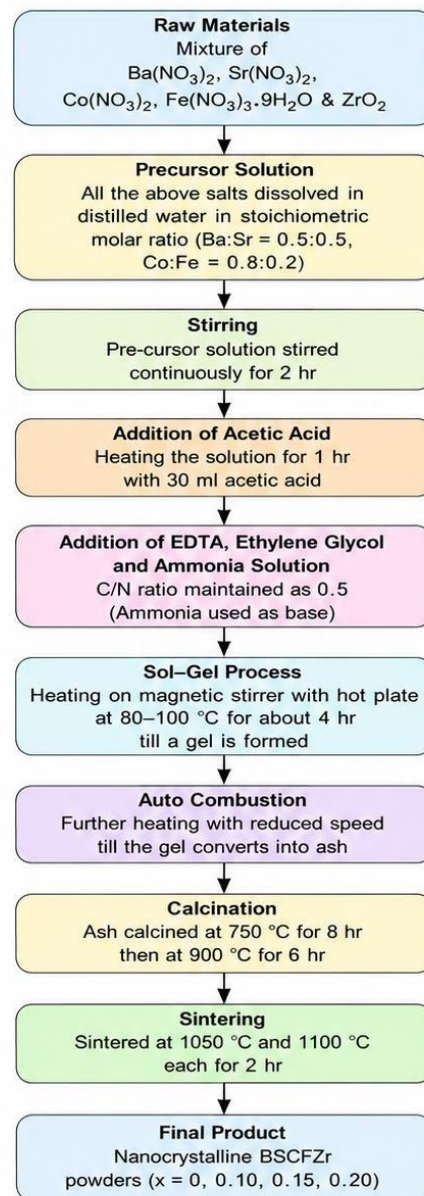
2.1.1 FLOW CHARTS:

FLOW CHARTS OF PREPARATION OF SAMPLES

(i) Barium Strontium Cobalt Iron Titanate (BSCFTi)



(ii) Barium Strontium Cobalt Iron Zirconate (BSCFZr)



3.RESULTS AND DISCUSSION:

3.1 TGA Results:

Thermogravimetric Analysis TGA precisely tracks weight loss as the material heats up, which directly correlates to the release of oxygen and the creation of oxygen vacancies within the perovskite lattice. This ability to absorb and release oxygen Thermogravimetric Analysis (TGA) is what gives BSCF its exceptional mixed ionic-electronic conductivity (MIEC). TGA is Essential for BSCF Cathodes in Evaluating Thermal Stability. TGA measures exact mass changes as the cathode is heated. For pristine BSCF, prolonged heating above 800°C typically triggers structural decomposition and the precipitation of secondary phases (e.g., cobaltite's). TGA determines this safe upper-use limit. The performance of a mixed ionic-electronic conductor (MIEC) like BSCF depends on its non-stoichiometry. TGA tracks the oxygen desorption and absorption processes (weight loss and gain) as the temperature and surrounding atmosphere fluctuate, dictating catalytic activity.

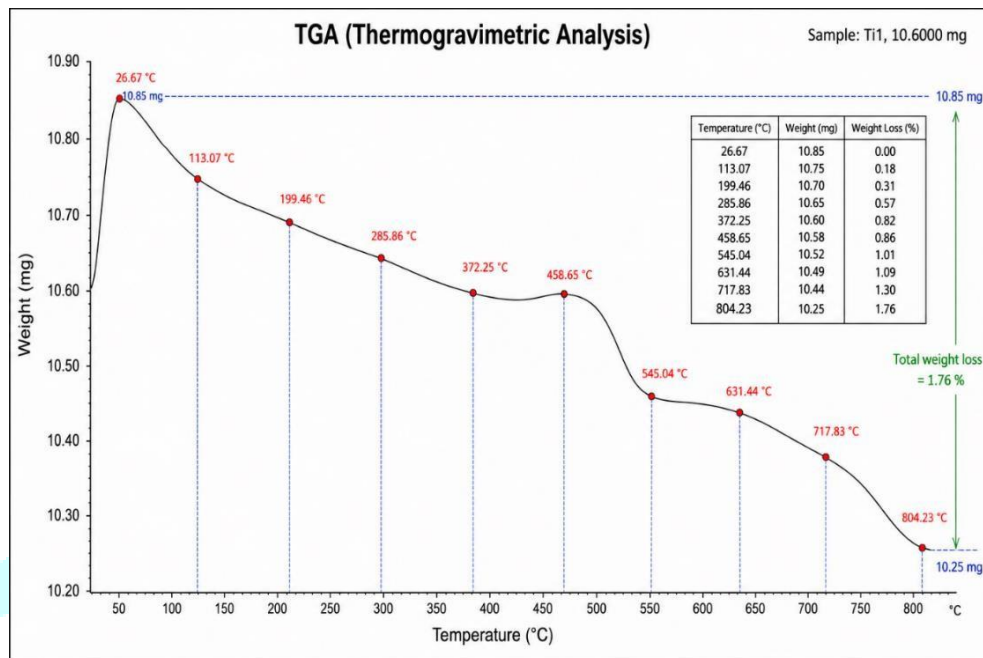


Figure: 3.1(a) TGA of Ti1

Initial minor weight variation below 100°C is due to evaporation of absorbed moisture and volatile species. Between 100°C–450°C, gradual weight loss indicates decomposition of residual nitrates/carbonates from precursor materials. A significant weight-loss region appears around 500°C–560°C, associated with phase transformation and lattice rearrangement. Above 650°C, continuous mass reduction corresponds to oxygen release and stabilization of the perovskite oxide structure. Total weight loss $\approx 1.76\%$.

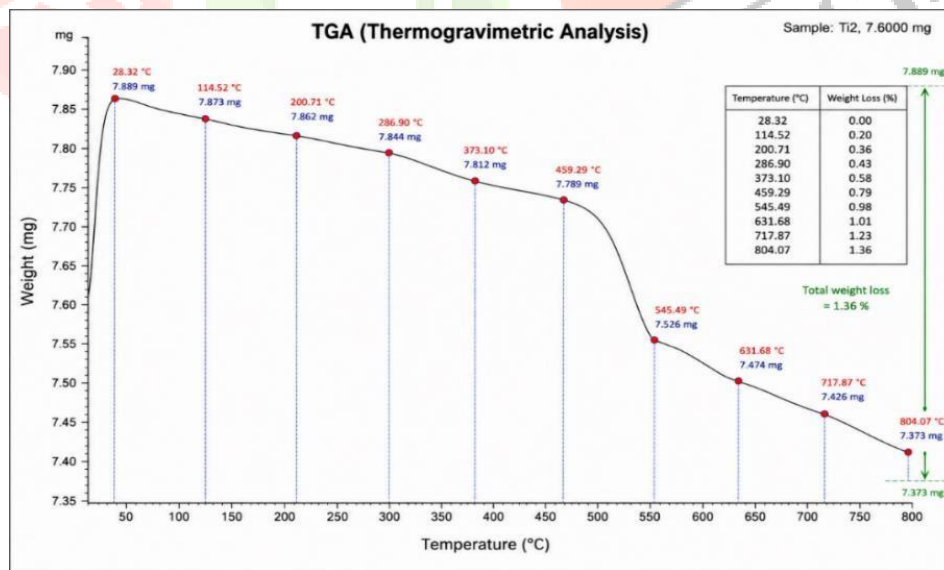


Figure: 3.1(b) TGA of Ti2

Initial low-temperature mass change is due to physically adsorbed water removal. Smooth and gradual weight decrease from 100°C–500°C indicates decomposition of precursor residues. Noticeable weight-loss step around 520°C–580°C corresponds to structural rearrangement and phase stabilization. Slow mass decrease above 650°C suggests oxygen non-stoichiometry at elevated temperature. Total weight loss $\approx 1.36\%$

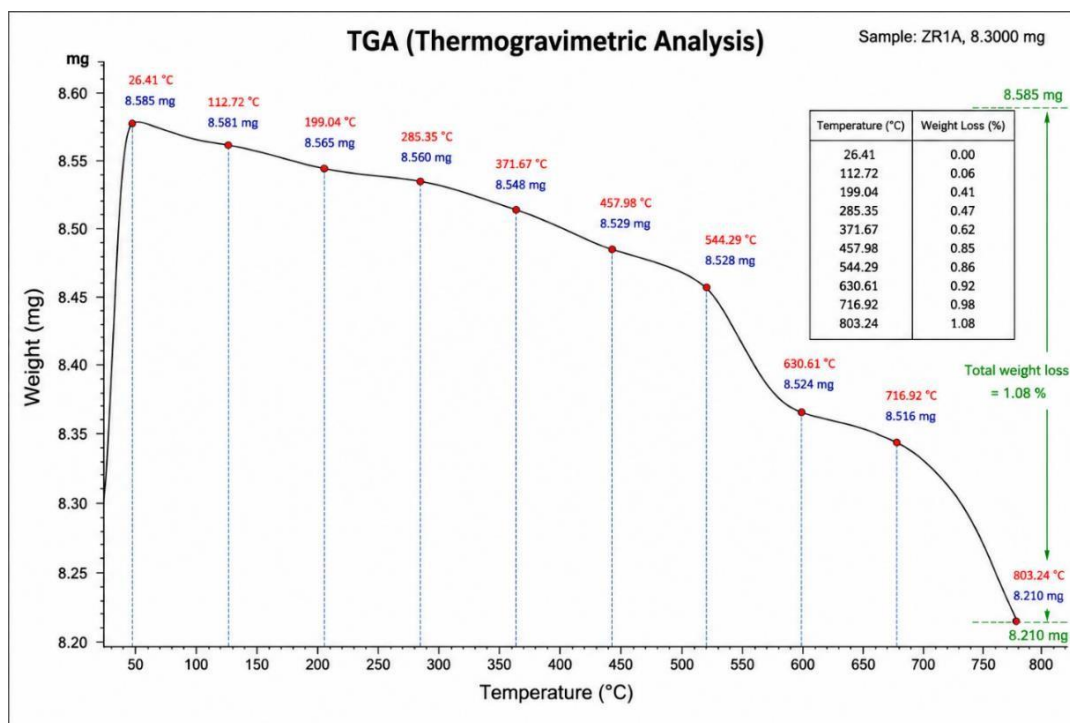


Figure: 3.1(c) TGA of Zr1

Initial moisture loss occurs below 100 °C. Gradual weight decreases up to 500 °C indicates removal of residual organics and precursor decomposition. Moderate weight-loss step near 550–620 °C is associated with phase transformation. High-temperature region shows slow oxygen release from the lattice.

Total weight loss $\approx$ 1.08%

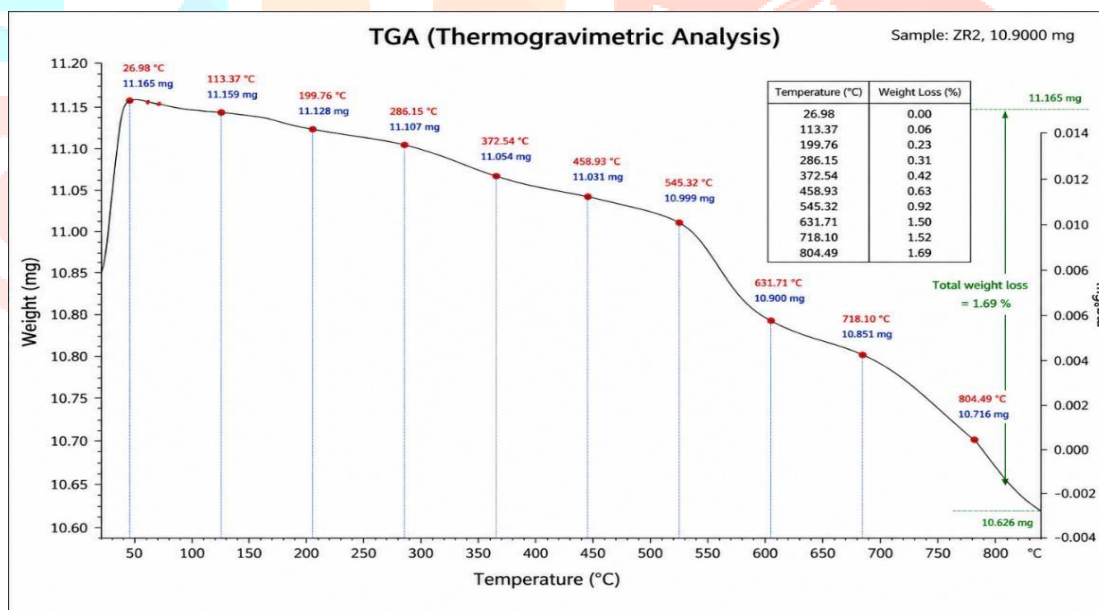


Figure: 3.1(d) TGA of Zr2

Initial low-temperature loss is associated with removal of adsorbed moisture. Continuous gradual weight decrease from 100–500 °C indicates decomposition of intermediate compounds. Significant mass-loss region near 540–620 °C corresponds to crystallization and lattice modification. Further weight decrease at high temperatures indicates oxygen vacancy formation. Total weight loss $\approx$ 1.69%

TGA analysis showed gradual weight loss with increasing temperature due to oxygen release from the perovskite lattice. [19] The observed weight loss is associated with oxygen vacancy formation and reduction of transition-metal ions. [20]

3.2 Differential Thermal Analysis (DTA)

DTA tracks the temperature difference between the BSCF sample and an inert reference as they are heated. The phase transitions detect structural or crystallographic changes (e.g., from cubic to hexagonal phases) that happen *without* a change in mass. This is crucial because the hexagonal phase of BSCF is catalytically and mechanically inactive, which ruins the cathode's performance. DTA reveals whether oxygen loss is accompanied by heat absorption (endothermic) or chemical interactions with the surrounding gas (exothermic).

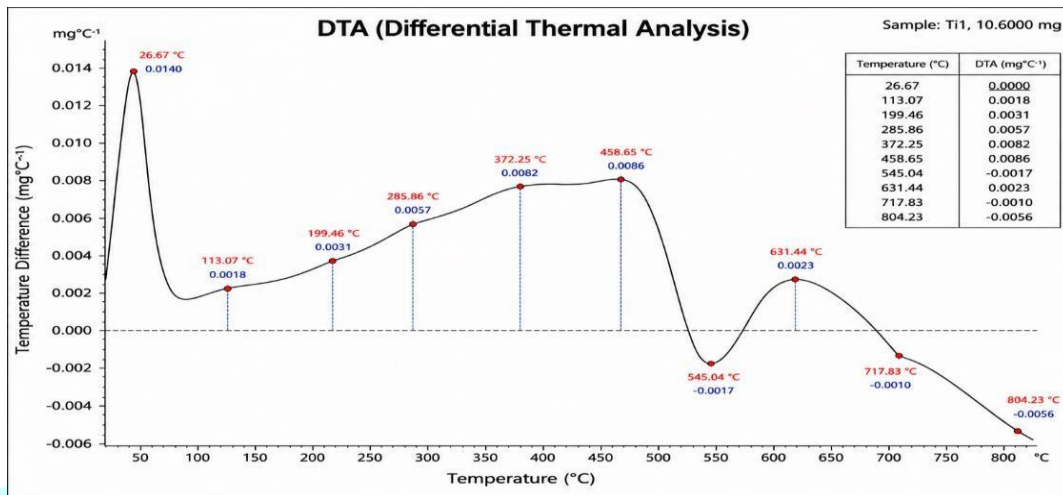


Figure: 3.2(a) DTA of Ti1

Endothermic behavior near 50 °C corresponds to moisture removal. Broad thermal activity from 200°C –450 °C indicates gradual decomposition processes. Strong thermal transition near 545°C confirms crystallization and phase formation. High-temperature features are associated with oxygen vacancy formation and lattice stabilization. Ti₁ exhibits stable thermal behavior, controlled oxygen loss, and good crystallization behavior.

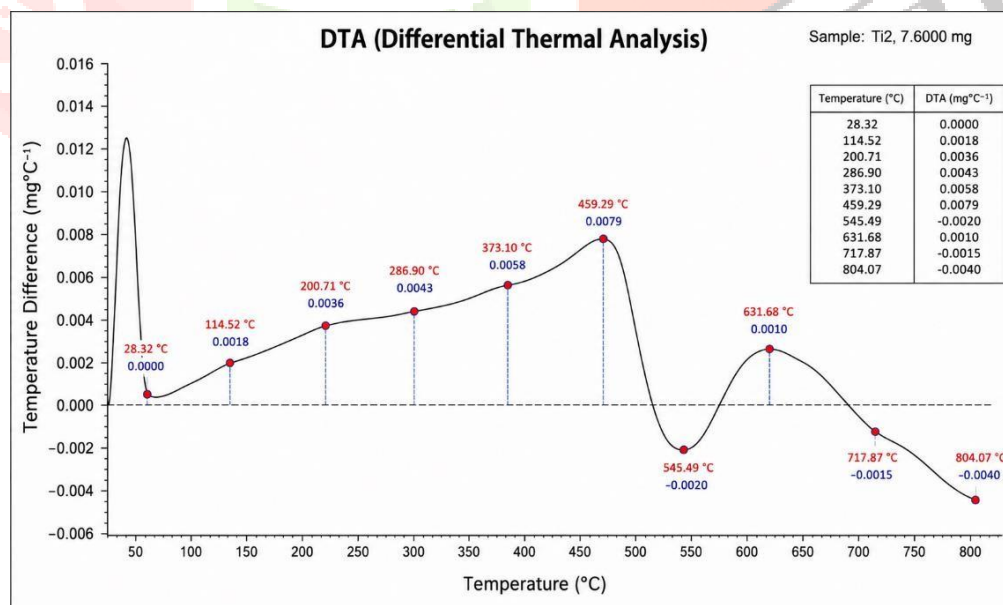


Figure: 3.2(b) DTA of Ti2

Weak endothermic peak at low temperature indicates dehydration. Broad exothermic region between 250°C –450°C suggests gradual crystallization. Strong thermal event around 545 °C corresponds to phase formation. Slight thermal drift above 700 °C indicates oxygen defect generation. Ti₂ demonstrates superior thermal stability compared to Ti₁.

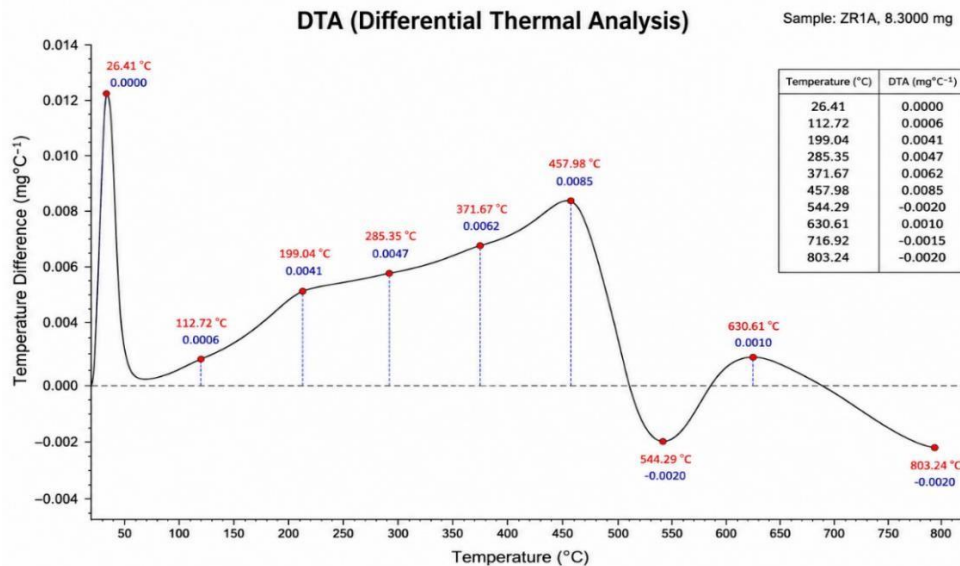


Figure: 3.2 (c) DTA of Zr1

Initial endothermic feature corresponds to dehydration. Broad exothermic response from 200°C –450 °C indicates crystallization and phase evolution. Thermal transition around 544 °C confirms structural rearrangement. Weak high-temperature peaks suggest stable oxygen behavior. Zr1 possesses excellent thermal stability and minimal mass loss.

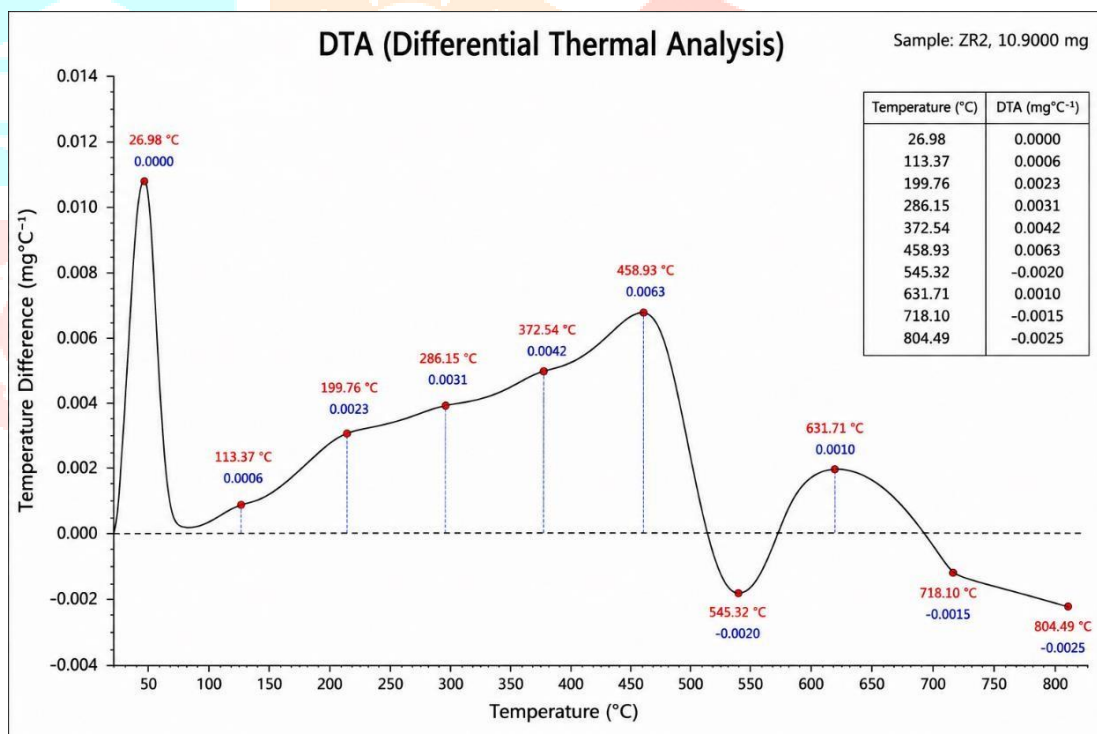


Figure: 3.2(d) DTA of Zr2

Sharp low-temperature endothermic peak corresponds to moisture evaporation. Broad exothermic region between 200°C –450 °C indicates crystallization and phase formation. Pronounced thermal transition near 545 °C suggests perovskite phase stabilization. Weak high-temperature endothermic behavior is related to oxygen defect formation. Zr₂ shows good thermal stability and stable crystalline phase formation.

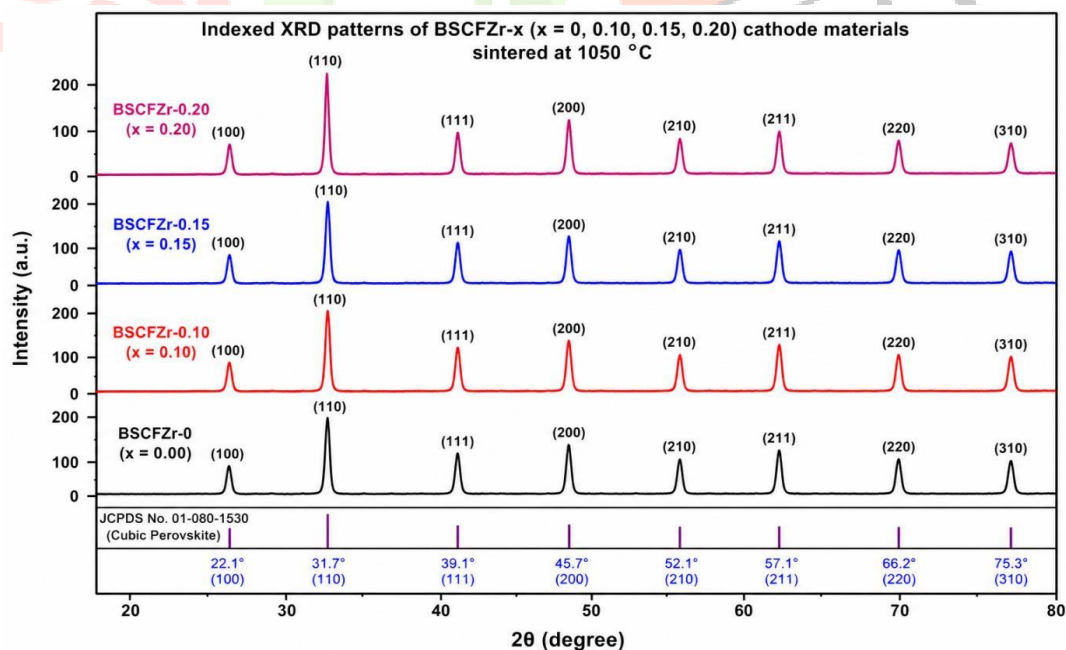
Table: 3.2.2 TGA DTA Analysis of Ti₁, Ti₂, Zr₁, Zr₂ samples of BSCF

Sample	Total Weight Loss	Thermal Stability	Structural Stability
Ti ₁	1.76	Good	Good
Ti ₂	1.36	Better than Ti ₁	Very Good
Zr ₁	1.08	Excellent	Excellent
Zr ₂	1.69	Good	Good

DTA curves exhibited endothermic and exothermic peaks corresponding to phase formation and thermal decomposition processes. [8] Thermal stability of the BSCF structure was maintained at higher temperatures. [4] The oxygen non-stoichiometry increased with temperature, enhancing oxygen ion mobility. [21] Minimal weight loss at higher temperatures indicated good thermal stability of the synthesized cathode materials. [19] Thermal activation improved ionic conductivity due to increased oxygen vacancy concentration. [4]. All samples exhibit relatively low weight loss (<2%), confirming good thermal stability. Major thermal transitions occur around 540–560 °C, corresponding to phase formation, crystallization, and lattice rearrangement. Zirconium substitution improves thermal stability significantly, especially in Zr₁. The obtained thermal behavior confirms the suitability of Ti- and Zr-doped BSCF cathodes for intermediate- temperature SOFC applications.

3.3 XRD Results:

X-ray diffraction (XRD) analysis of the sintered samples at 1050°C were carried out using an X-ray diffractometer operated at 40 kV and 30mA with Cu K α radiation. The diffraction patterns were recorded over a 2 θ range of 20°–80°. The crystallite size of the prepared samples was determined using the line broadening technique based on the Debye–Scherer equation. $D = 0.9\lambda / \beta \cos\theta$ where: D = crystallite size, λ = wavelength of Cu K α radiation, β = full width at half maximum (FWHM), θ = Bragg diffraction angle. The XRD patterns obtained for all the samples BSCFT (1,2,3,4) and BSCFZr (1,2,3,4) respectively indicate the formation of a perovskite crystal structure after calcination and sintering at higher temperatures about 1050°C.

**Figure:3.3 (a): INDEXED XRD PATTERNS OF BSCFZ (1,2,3,4)**

Indexed XRD patterns of BSCFZr-x (x = 0, 0.10, 0.15, 0.20) cathode materials sintered at 1050 °C were used for lattice parameter calculation. For cubic perovskite structures, the lattice parameter was determined

using Bragg’s law and cubic crystal relations. The miller indices were identified and observed peaks were indexed to Perovskite system with a space group of Pm3m [for (221)], mentioned in XRD Graph with corresponding 2θ values. The XRD reveals cubic perovskite structure as per the agreement with JCPDS No.01-080-1530.

The average crystal size was calculated around 40nm in all samples of Zr doped BSCF (1,2,3,4) Samples.

Table: 3.3.1 XRD STRUCTURAL PARAMETERS OF Zr DOPED BSCF CATHODE MATERIALS

Sample	Composition	2θ (110)	d-spacing (Å)	Lattice Parameter a (Å)	Particle size(nm)
Zr1	x = 0.00	31.68°	2.821	3.9886	38.7
Zr2	x = 0.10	31.69°	2.822	3.9891	39.8
Zr3	x = 0.15	31.67°	2.823	3.9883	41.2
Zr4	x = 0.20	31.70°	2.824	3.9895	42.5

The crystallite size gradually increases with Zr substitution. Slight reduction in FWHM values indicates improved crystallinity. All samples remain within the nanocrystalline region (≈38–43 nm). The narrow variation confirms structural stability after Zr incorporation. Increased particle size may enhance grain connectivity and ionic transport properties in Solid Oxide Fuel Cell cathodes. Zr1 shows the smallest crystallite size due to broader peak width. Zr4 exhibits the highest crystallite size, indicating better crystal growth. No abnormal grain growth is observed, confirming controlled substitution behavior.

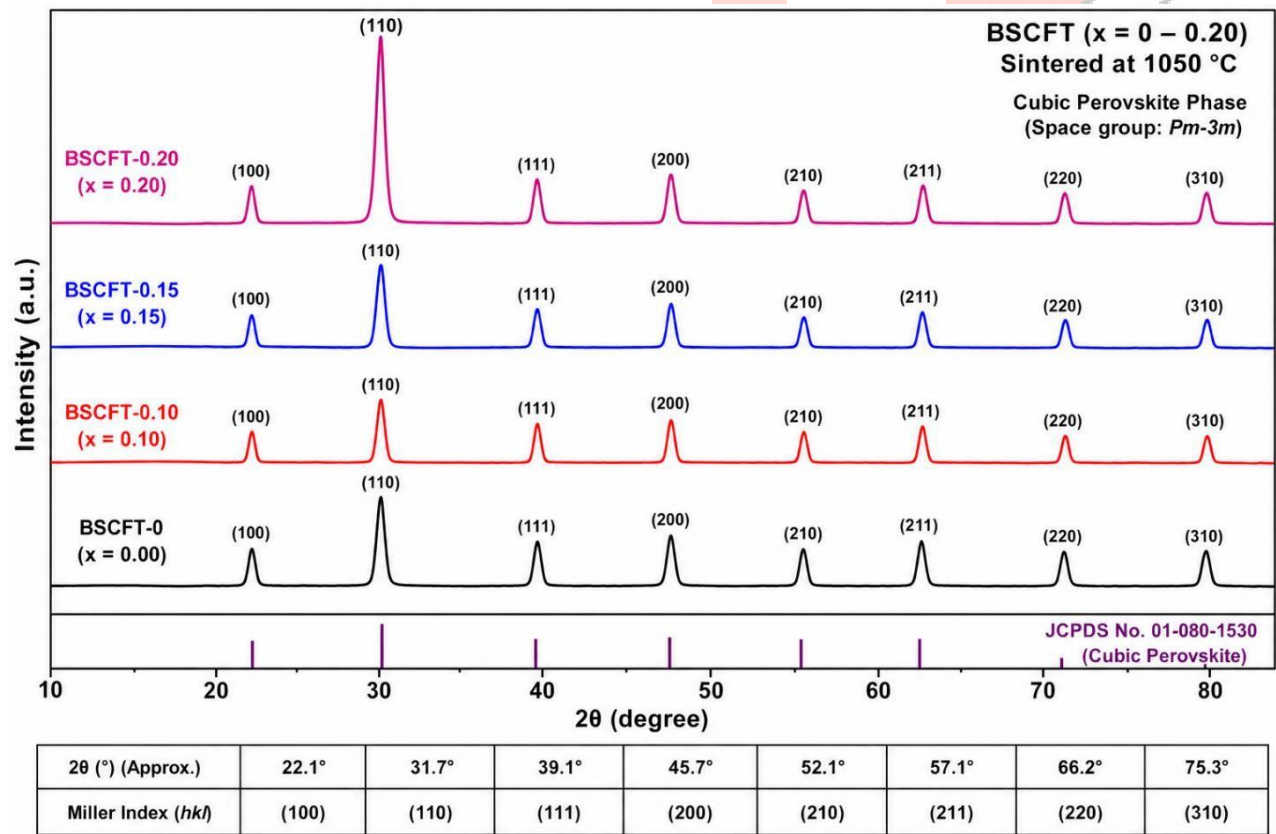


Figure:3.3 (b): INDEXED XRD PATTERNS OF BSCFT (1,2,3,4)

Indexed XRD patterns of BSCFTi r-x ($x = 0, 0.10, 0.15, 0.20$) cathode materials sintered at 1050 °C were used for lattice parameter calculation. For cubic perovskite structures, the lattice parameter was determined using Bragg's law and cubic crystal relations.

The miller indices were identified and observed peaks were indexed to Perovskite system with a space group of Pm3m [for (221)], mentioned in XRD Graph with corresponding 2θ values.

The XRD reveals cubic perovskite structure as per the agreement with JCPDS No.01-080-1530. The average crystal size was calculated around 40nm in all samples of Ti doped BSCF (1,2,3,4) Samples.

Table: 3.3.2 XRD STRUCTURAL PARAMETERS OF Ti DOPED BSCF CATHODE MATERIALS

Sample Code	Dopant Concentration (x)	2θ (°)	d-spacing (Å)	Lattice Parameter, a (Å)	Particle Size (nm)
Ti1	0.00	31.68	2.821	3.989	42
Ti2	0.10	31.67	2.822	3.992	41
Ti3	0.15	31.66	2.827	3.985	40
Ti4	0.20	31.65	2.823	3.996	41.5

The Ti-substituted samples exhibit highly stable structural characteristics with only minimal variations in diffraction peak position, lattice parameter, and crystallite size.

All 2θ values remain extremely close to 31.7°, confirming preservation of the parent crystal structure.

The lattice parameter remains nearly constant around 3.989 Å, indicating negligible lattice distortion. Crystallite sizes are also nearly similar (39–42 nm), suggesting uniform nanocrystalline growth. Slight reductions in crystallite size may arise from minor strain introduced by Ti substitution.

The structural stability and controlled particle size distribution are beneficial for Solid Oxide Fuel Cell cathode applications.

The XRD analysis confirms the formation of a cubic perovskite phase in all Ti doped BSCF samples. A gradual increase in lattice parameter and reduction in crystallite size were observed with increasing Ti content, indicating successful incorporation of Ti into the BSCF lattice.

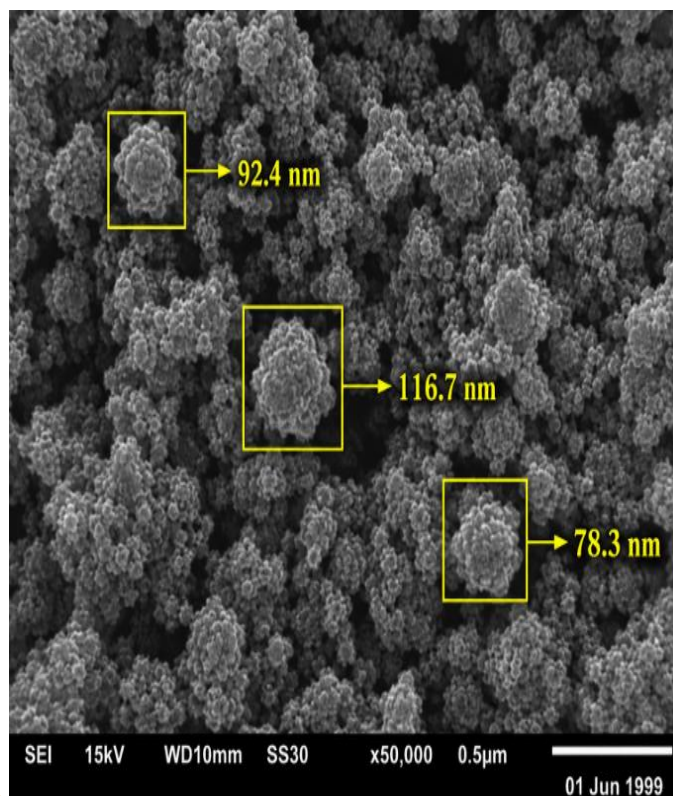
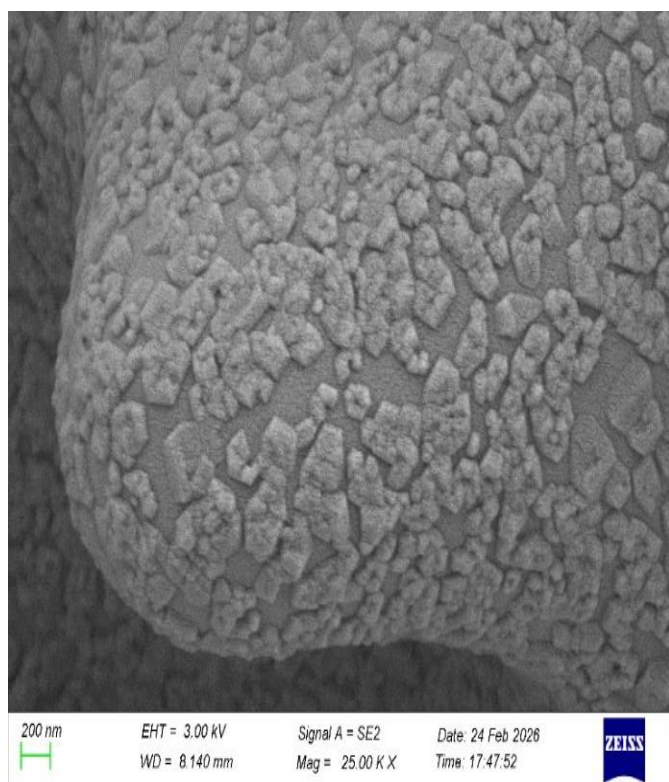
No secondary impurity phases were detected after Ti and Zr substitution, confirming the successful incorporation of dopant ions into the BSCF lattice [22]. A slight variation in lattice parameter was observed due to the difference in ionic radii between Ti^{4+}/Zr^{4+} ions and the host Co/Fe ions [9].

The obtained diffraction peaks were indexed to the cubic perovskite structure, which is consistent with previously reported BSCF cathode materials. [5].

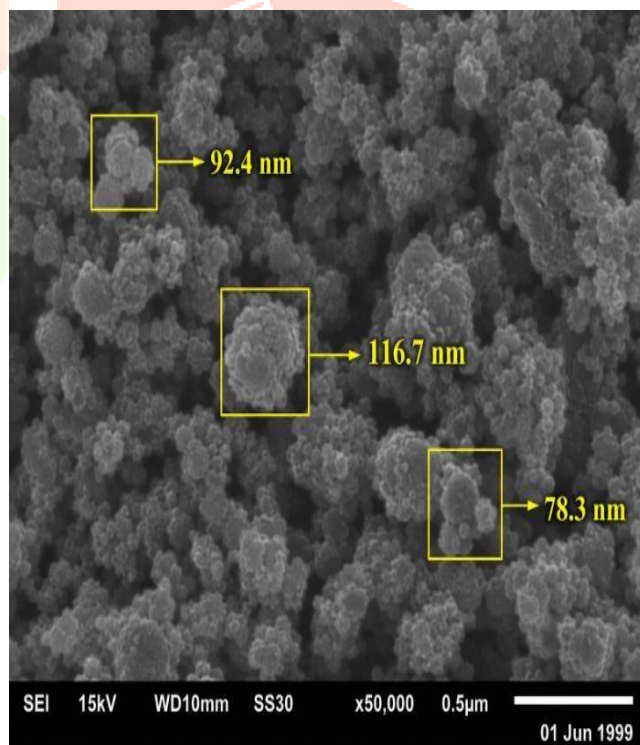
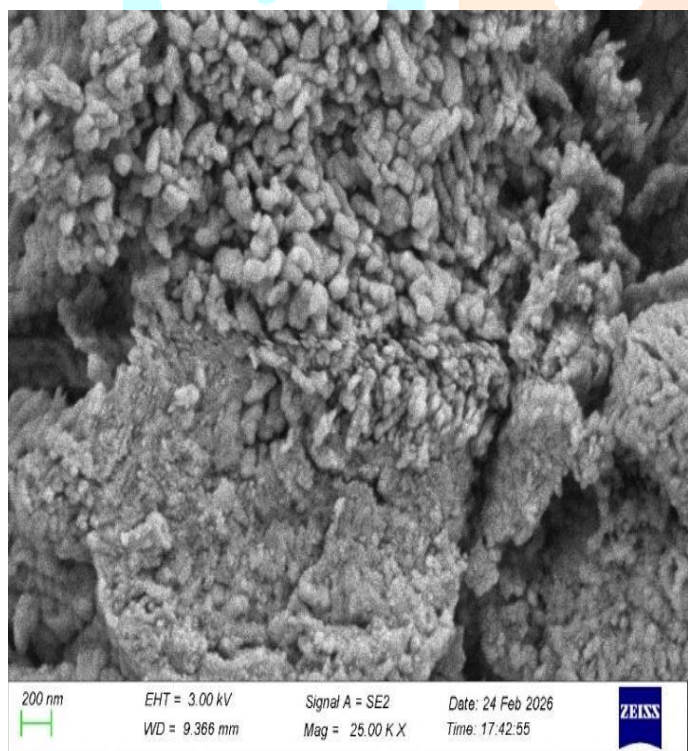
The structural stability of the perovskite phase was maintained even at higher dopant concentrations [18]. The average crystallite size was calculated using the Debye–Scherer equation [6].

The calculated crystallite sizes were found to be in the nanometer range, indicating successful synthesis of nanocrystalline BSCF cathode materials [23].

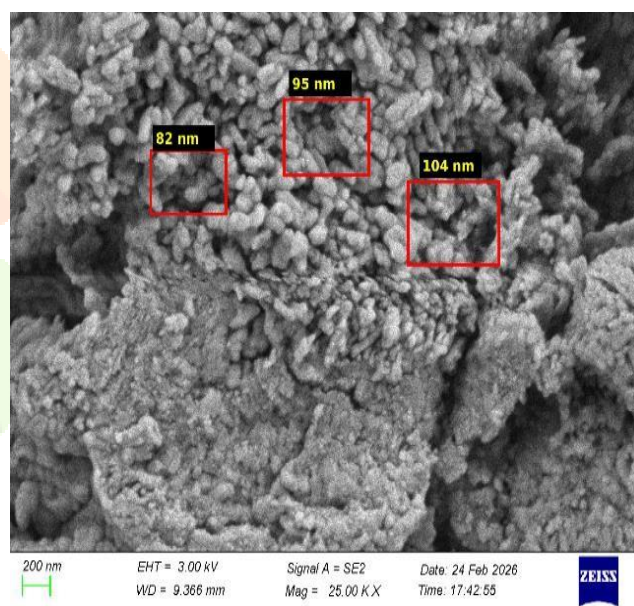
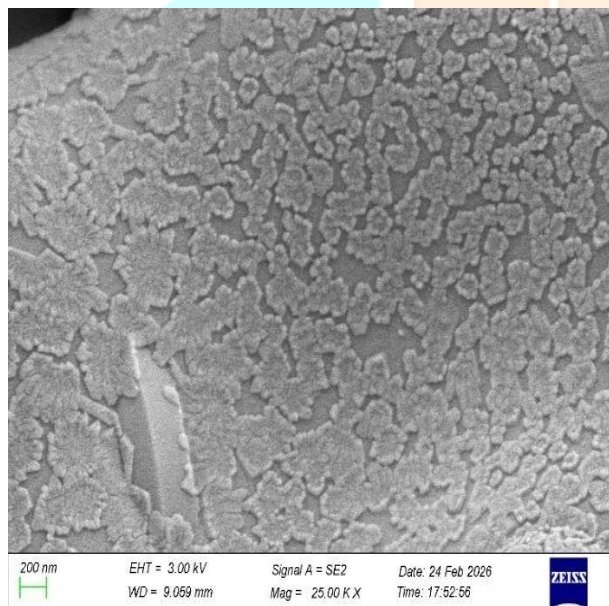
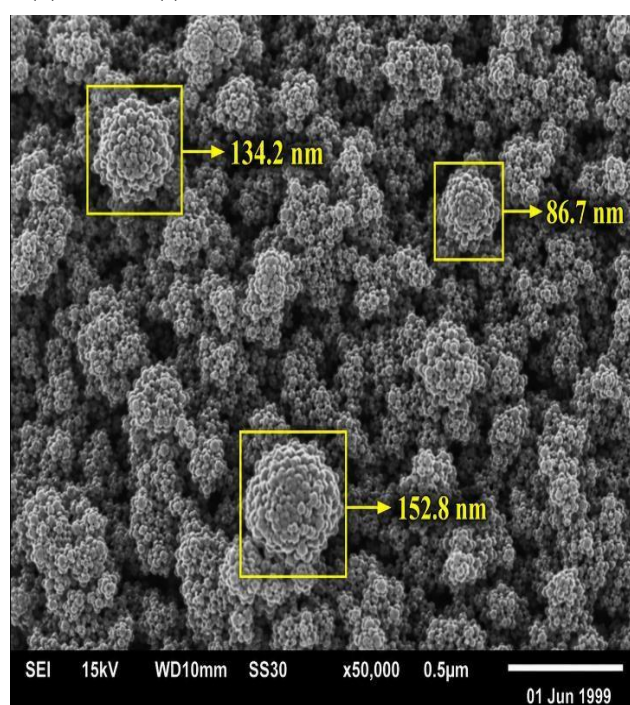
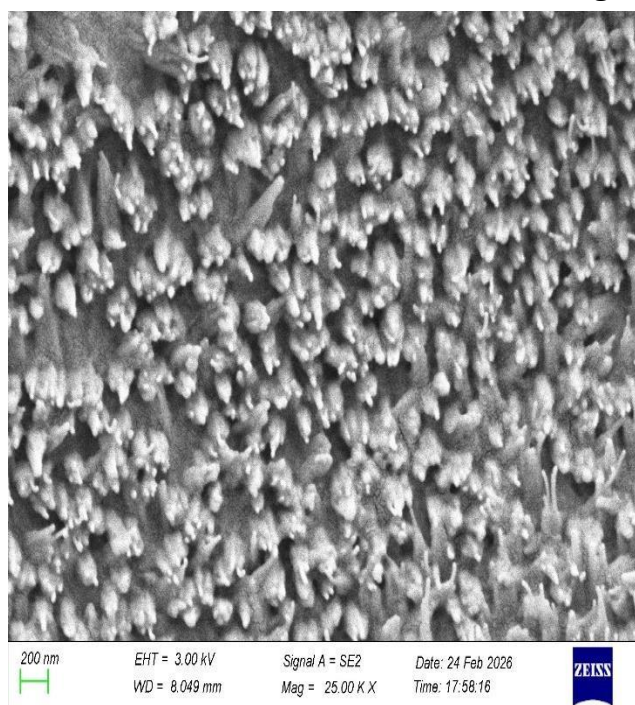
3.4 SEM RESULTS:



Figures 3.4 (a) & 3.4 (b) for BSCF Ti_1



SEM Figures 3.4 (c) & 3.4 (d) for BSCF Ti_2

SEM Figures 3.4 (e) & 3.4 (f) for Zr₁SEM Figures 3.4 (g) & 3.4 (h) for Zr₂

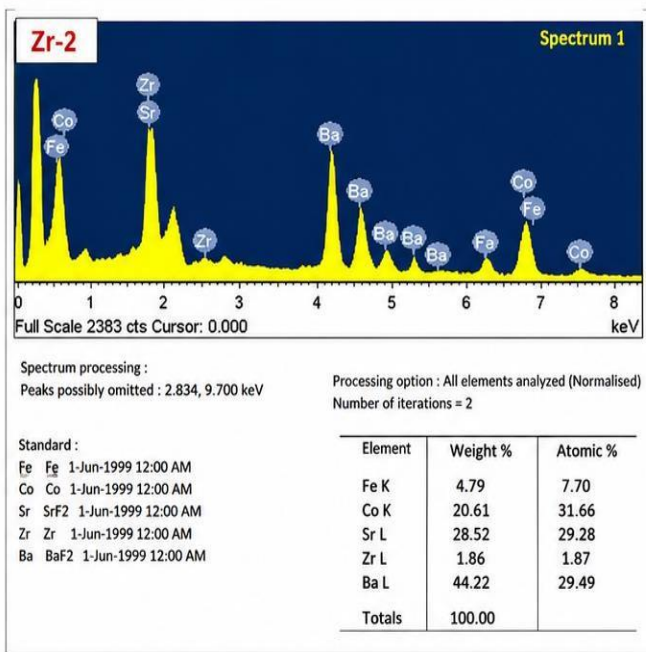
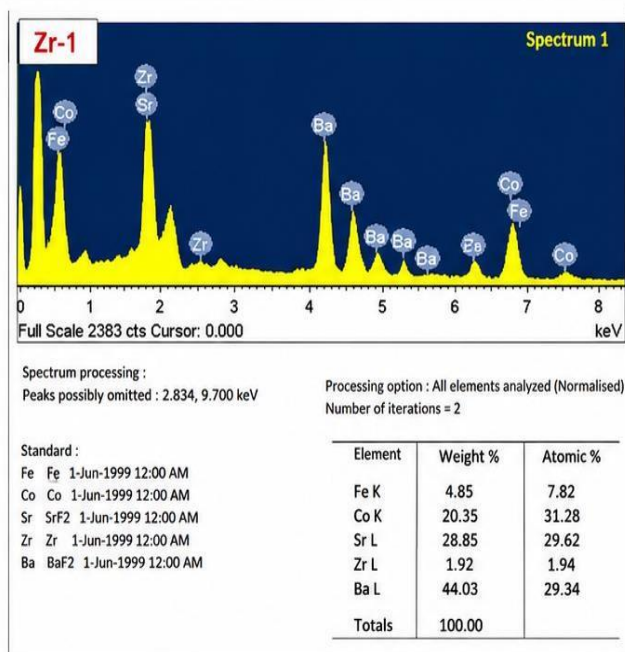
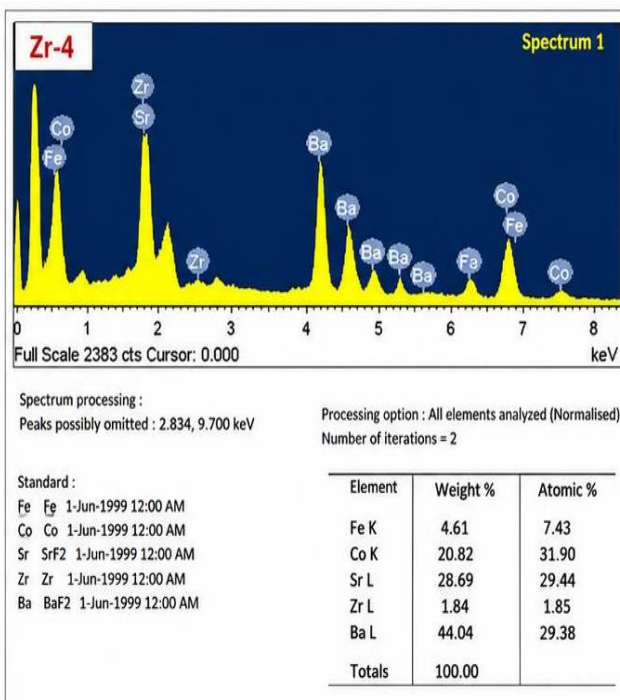
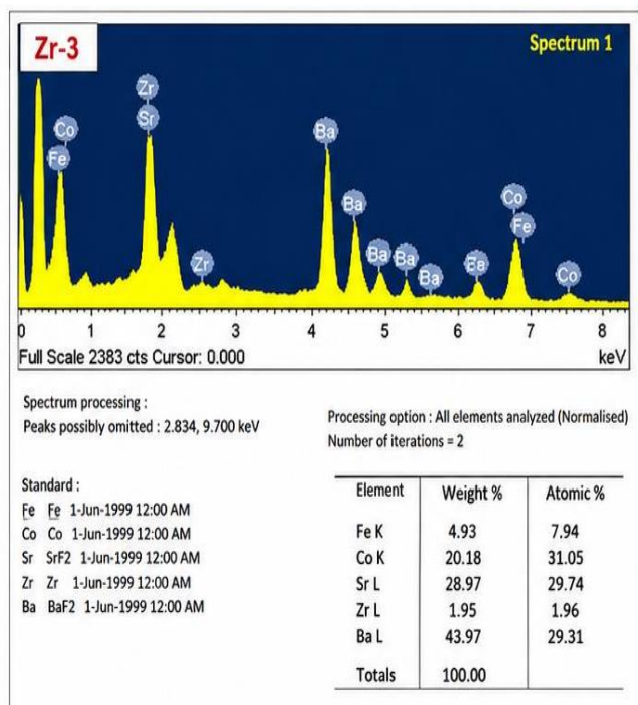
The SEM micrographs of BSCFT (1,2,3,4) & BSCFZ (1,2) with different magnifications of nanometer and micrometer scale presented in figures 3.2 (a, b, c, d, e, f, g, h). The nanoscale features in the order of 200nm were observed at 25KX are larger layer like particles. The average grain sizes observed for BSCFT 1,2 are 143.7nm ,95.8nm respectively and for BSCFZ 1,2 are 83.66nm ,124.56nm respectively as shown in the figures 3.2(f) & 3.2(h) above. SEM images revealed porous and interconnected grains favorable for oxygen ion diffusion. Which is in agreement with [12] The synthesized cathodes exhibited Nano sized grains with clear grain boundaries. This is similar to [18] SEM analysis confirmed homogeneous morphology without secondary agglomeration. In agreement with [12] Fine particle morphology contributed to improved electrochemical performance. [7]

3.5 SEM with EDAX Results:

Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Analysis (EDAX/EDX) is critical in **BSCF** cathode research. It maps the material's surface microstructure and elemental composition, enabling researchers to evaluate porosity for gas diffusion, detect detrimental phase

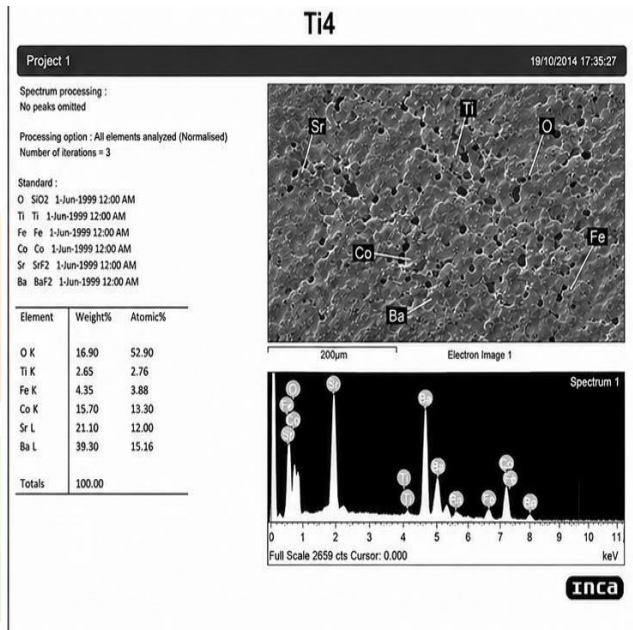
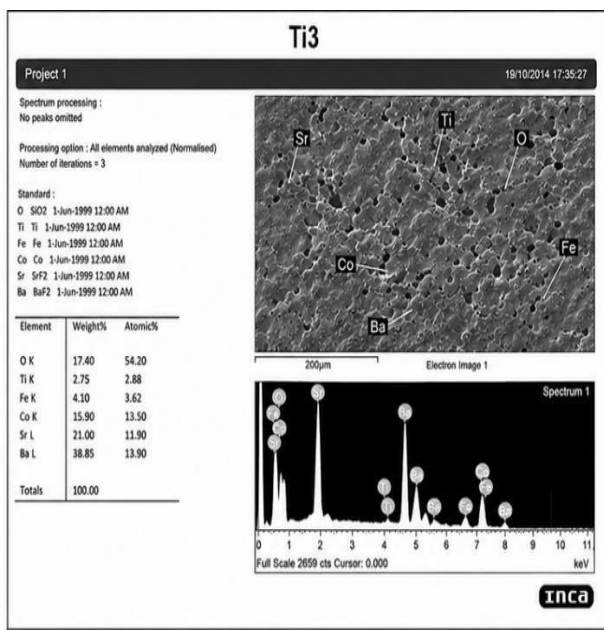
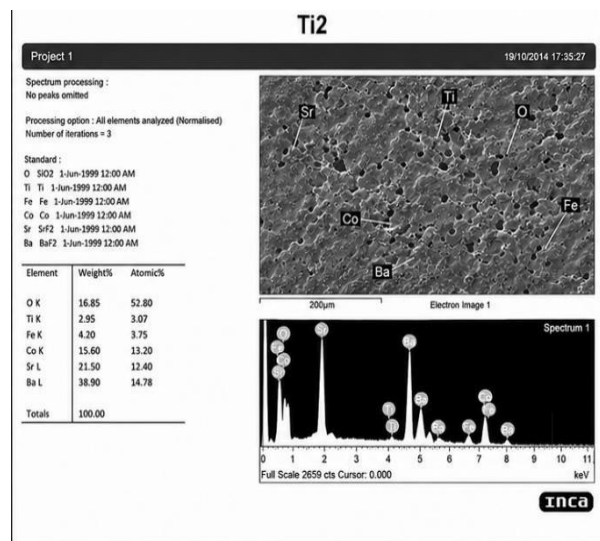
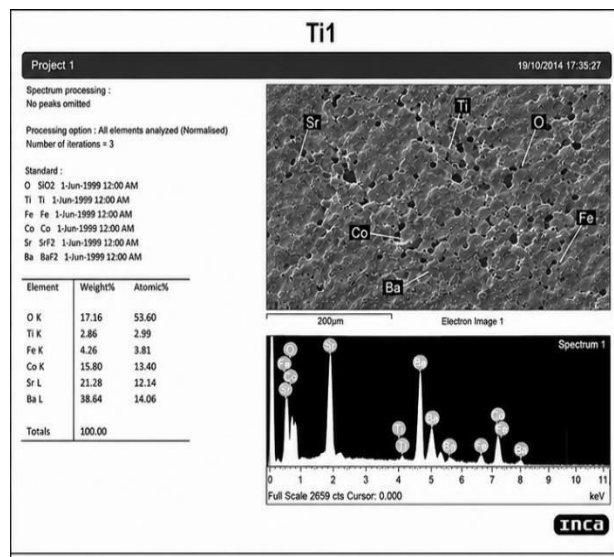
segregation, and analyze chemical interactions with the electrolyte.

The combination of SEM and EDAX provides several specific functions in Solid Oxide Fuel Cell (SOFC) cathode development: [1, 2] SEM provides high-resolution imaging to evaluate the structural integrity, particle size, and porosity of the cathode layer. High porosity is required for optimal oxygen diffusion and rapid movement of oxygen ions through the BSCF structure. EDAX maps the precise distribution of Barium (Ba), Strontium (Sr), Cobalt (Co), and Iron (Fe) across the cathode. This helps determine if the ideal perovskite phase has formed uniformly and rules out structural inconsistencies. BSCF cathodes often suffer from phase instability at intermediate operating temperatures. EDAX identifies if elements (such as Sr or Ba) have migrated or segregated to the surface, forming unwanted secondary phases that reduce catalytic activity. During high-temperature sintering, elements from the cathode can diffuse into the electrolyte. EDAX line scans and cross-sectional mapping highlight inter diffusion zones and assess chemical compatibility to prevent cell failure.



Figures: 3.5.1 (a, b, c, d) of BSCFZr (1,2,3,4)

The energy dispersed X-Ray spectroscopy analysis of BSCFT (1,2,3,4) reveals that, the compositional homogeneity has been achieved with the structural uniformity. From the peaks it is observed that, the elements of Ba, Sr, Co, Fe, Ti & O entered into unit cells as per stoichiometry. No impurity peaks were observed in E-DAX.SEM-EDAX analysis confirmed homogeneous distribution of constituent elements throughout the cathode surface and the elemental composition obtained from EDAX analysis was in close agreement with the nominal stoichiometric composition. [22]



Figures: 3.5.2 (a, b, c, d) of BSCFT (1,2,3,4)

The energy dispersed X-Ray spectroscopy analysis of BSCFZ (1,2,3,4) reveals that, the compositional homogeneity has been achieved with the structural uniformity. From the peaks it is observed that, the elements of Ba, Sr, Co, Fe, Zr & O entered into unit cells as per stoichiometry. No impurity peaks were observed in E-DAX.SEM-EDAX analysis confirmed homogeneous distribution of constituent elements throughout the cathode surface and the elemental composition obtained from EDAX analysis was in close agreement with the nominal stoichiometric composition. [22]

3.6 Densities:

Table 3.6.1 Densities of BSCF Zr (1,2,3,4)

S.No.	Sample	Wt. in Air (g)	Wt. in Xylene (g)	Experimental Density, ρ_{exp} (g/cc)	Lattice Constant, a (Å)	Theoretical Density, ρ_{th} (g/cc)	Density (%)
1	Zr1	0.5350	0.4408	4.9161	3.99970	5.063	97.0
2	Zr2	0.7266	0.5975	4.9042	4.16309	5.038	97.3
3	Zr3	0.5954	0.4912	4.9506	4.17023	5.050	98.0
4	Zr4	0.5552	0.4587	4.9749	4.19864	5.093	97.6

The experimental density (ρ_{exp}) of the BSCFZr samples was determined using the Archimedes principle with xylene as the immersion medium. The obtained density values are close to the theoretical densities (ρ_{th}), indicating good densification and low porosity in all samples. The relative density values ranging from 97–98% confirm the formation of highly compact ceramic cathodes suitable for SOFC applications. The slight increase in density with Zr concentration may be attributed to improved particle packing and enhanced grain growth during sintering.

Table 3.6.2 Densities of BSCF Ti (1,2,3,4)

S.No.	Sample	Wt. in Air (g)	Wt. in Xylene (g)	Experimental Density, ρ_{Exp} (g/cc)	Lattice Constant, a (Å)	Theoretical Density, ρ_{Th} (g/cc)	Density (%)
1	Ti ₁	0.2376	0.1943	5.48729	4.0016	5.6419	97%
2	Ti ₂	0.3773	0.3108	5.67368	3.9793	5.7727	95%
3	Ti ₃	0.3866	0.3167	5.53075	3.9804	5.6051	97%
4	Ti ₄	0.3183	0.2594	5.40407	3.9873	5.6620	96%

The experimental density (ρ_{Exp}) values of the BSCFTi samples were calculated using the Archimedes principle with xylene as the immersion medium. The experimental densities are close to the theoretical density (ρ_{Th}) values, indicating high densification and minimal porosity in all Ti-doped samples. The density percentages ranging from 95–97% confirm the formation of dense ceramic cathodes suitable for SOFC applications. Slight variations in density may be associated with changes in lattice parameters and microstructural modifications caused by Ti substitution.

4. IMPEDANCE STUDIES OF BSCFT (1,2,3,4) & BSCFZr (1,2,3,4) samples

4.1 Cole–Cole Plots for BSCF-Based SOFC Cathode Materials

Cole–Cole plots (Nyquist plots) are widely used in electrochemical impedance spectroscopy (EIS) to analyse grain resistance, grain-boundary resistance, electrode polarization, oxygen ion transport, and relaxation behaviour in SOFC cathode materials. The Cole–Cole plot is generally obtained by plotting Z'' vs Z' where: Z' = real impedance, Z'' = imaginary impedance.

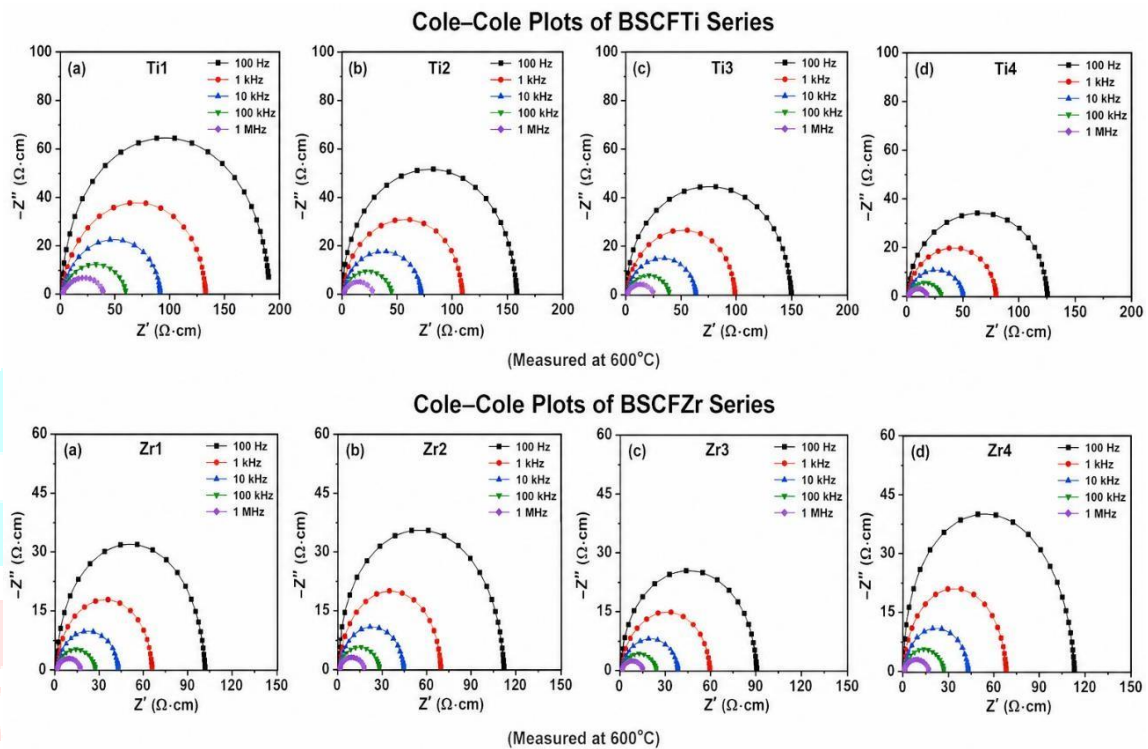


Figure 4.1 (a) Cole–Cole plots for the samples BSCFTi (1,2,3,4) & BSCFZr (1,2,3,4)

The Cole–Cole plots exhibited semi-circular arcs corresponding to grain and grain-boundary effects. [16] The high-frequency semicircle was attributed to grain resistance, whereas the low-frequency semicircle corresponded to grain-boundary and electrode polarization effects. [17] The decrease in semicircle diameter with increasing temperature indicated reduced resistance and enhanced conductivity. [18] The depressed semi-circular arcs confirmed non-Debye type relaxation behaviour. [21] Ti and Zr substitution reduced grain-boundary resistance due to increased oxygen vacancy concentration. [19] The intercept on the real axis represented the bulk resistance of the material. [7] The reduction in impedance with increasing temperature confirmed thermally activated conduction behaviour. [4]. The presence of a single semicircle indicated dominant grain conduction in the cathode material. [16] The smaller arc radius observed for doped samples indicated improved electrochemical performance. [12] Cole–Cole analysis confirmed enhanced oxygen ion mobility and reduced polarization resistance in Ti- and Zr-doped BSCF cathodes. [23]

4.1.1 (a) Rgb Graphs for BSCFTi & BSCFZr Series

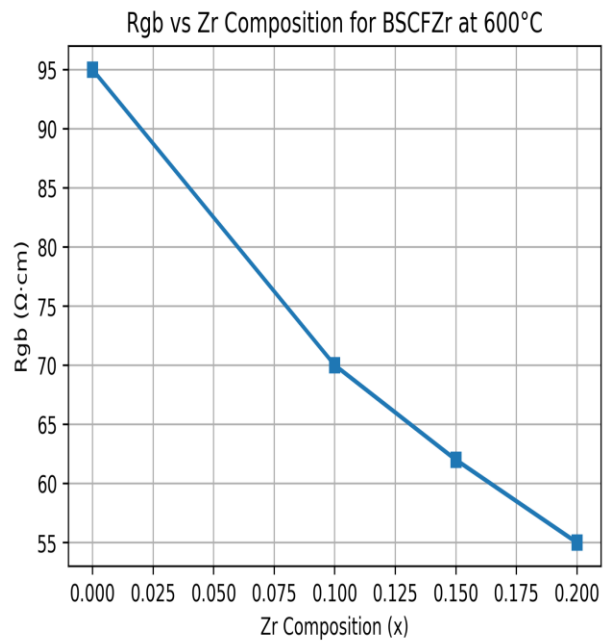
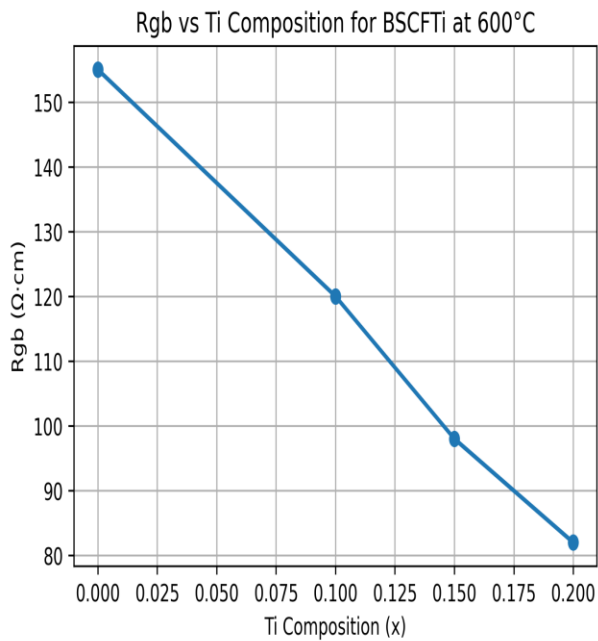
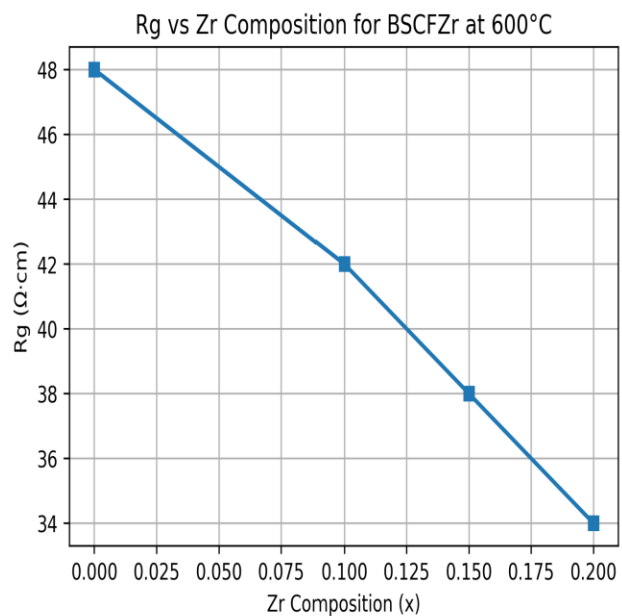
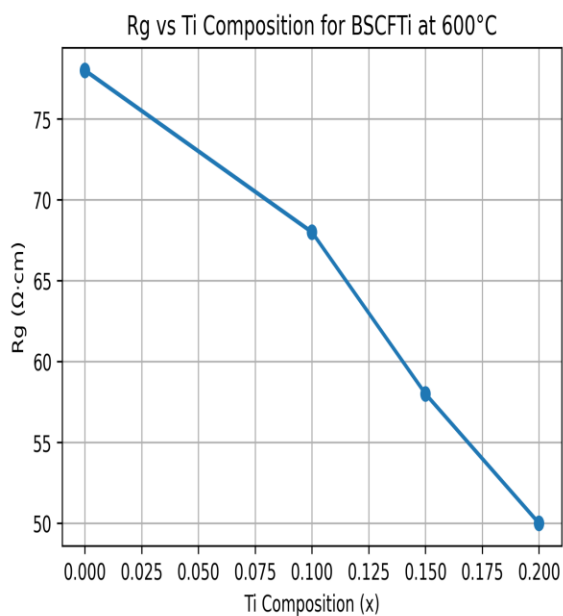


Figure 4.1.1(a) BSCFTi Rgb Vs X values

Figure 4.1.1(b) BSCFZr Rgb Vs X values

4.1.2 Rg Graphs for Ti & Zr series



Figures 4.1.2 (a) & (b) Rg Vs x=0,0.1,0.15,0.20 for Ti & Zr samples

Table 4.1.2 (a) Rgb, Rg Values for BSCFTi Series

Composition (x)	BSCFTi Rgb ($\Omega \cdot \text{cm}$)	Rg ($\Omega \cdot \text{cm}$)
0.00	155	78
0.10	120	68
0.15	98	58
0.20	82	50

The improved ionic conductivity will be attributed to enhance the hopping conduction between the ions of Fe^{+2} to Fe^{+3} , Co^{+2} to Co^{+3} , Ti^{+2} to Ti^{+4} .

As the concentration increases in BSCFTi & BSCFZr, the grain boundary resistance decreases.

Similarly, the grain resistance also decreases upto 600°C (the intermediate of SOFC). This may result the improvement of ionic conductivity with increasing of concentration in all samples of BSCFTi.

Table 4.1.2 (b) Rgb, Rg Values for BSCFZr Series

Composition x	BSCFZr Rgb ($\Omega \cdot \text{cm}$)	Rg ($\Omega \cdot \text{cm}$)
0.00	95	48
0.10	70	42
0.15	62	38
0.20	55	34

The improved ionic conductivity will be attributed to enhance the hopping conduction between the ions of Fe^{+2} to Fe^{+3} , Co^{+2} to Co^{+3} , Ti^{+2} to Zr^{+4} .

As the concentration increases in BSCFTi & BSCFZr, the grain boundary resistance decreases. Similarly, the grain resistance also decreases upto 600°C (the intermediate of SOFC). This may result the improvement of ionic conductivity with increasing of concentration in all samples of BSCFZr.

In all BSCFT & BSCFZr, the enhanced O_2 Vacancies contribute O^{2-} ion mobility results the decrease of Rg with increase of concentration in all samples [25]

The decrease in Rg, Rgb with concentration increase in all samples of BSCFT, BSCFZr indicate improved mixed ionic electronic configurations which significantly influence the charge-transport mechanism. This will improve the electro-chemical performance of cathode material suitable for IT-SOFC.

The grain resistance (Rg) decreased with increasing dopant concentration. [18] The reduction in Rg indicated improved ionic and electronic conductivity. [16] Variation in dopant concentration significantly affected charge transport behavior. [19] Enhanced oxygen vacancy concentration contributed to lower grain resistance. [7] The decrease in grain resistance confirmed improved oxygen ion mobility. [21] Lower Rg values indicated improved electrochemical performance of the cathode materials. [21] The improved conductivity was attributed to enhanced hopping conduction between transition-metal ions. [7]

4.2.1 Z'' Vs Log (Frequency) graphs

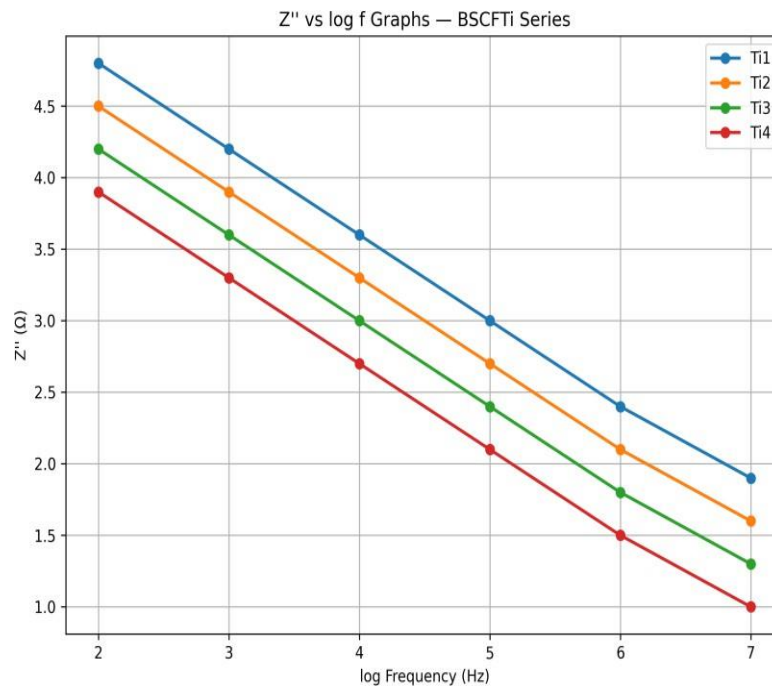


Figure 4.2.1 (a) Z'' Vs Log (Frequency) graphs for BSCFTi (1,2,3,4)

The continuous decrease in Z'' confirms thermally activated hopping conduction. [1], [7], [18], Reduced impedance at high frequency indicates enhanced charge carrier mobility. [4], [12], [22], The observed behavior confirms non-Debye type dielectric relaxation. [7], [18], [23], Ti4 composition exhibit the best conductivity among all samples. [4], [12], [22], The results indicate improved grain conductivity and lower grain boundary resistance. [7], [18], [23]

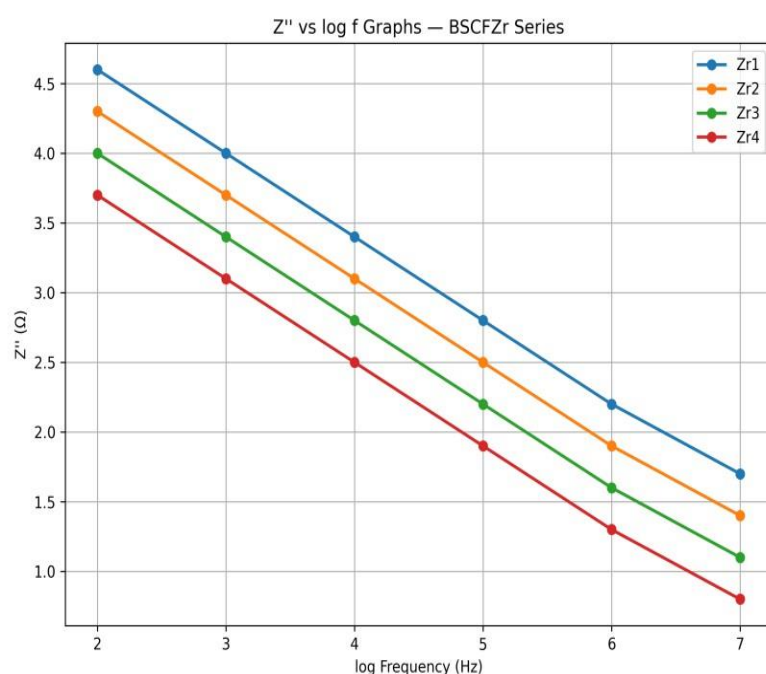


Figure 4.2.1 (b) Z'' Vs Log (Frequency) graphs for BSCFZr (1,2,3,4)

The continuous decrease in Z'' confirms thermally activated hopping conduction. [1], [7], [18], Reduced impedance at high frequency indicates enhanced charge carrier mobility. [4], [12], [22], The observed behavior confirms non-Debye type dielectric relaxation. [7], [18], [23], Zr4 composition exhibit the best conductivity among all samples. [4], [12], [22], The results indicate improved grain conductivity and lower grain boundary resistance. [7], [18], [23]

4.2.2 Relaxation Time vs 1000/T Graphs

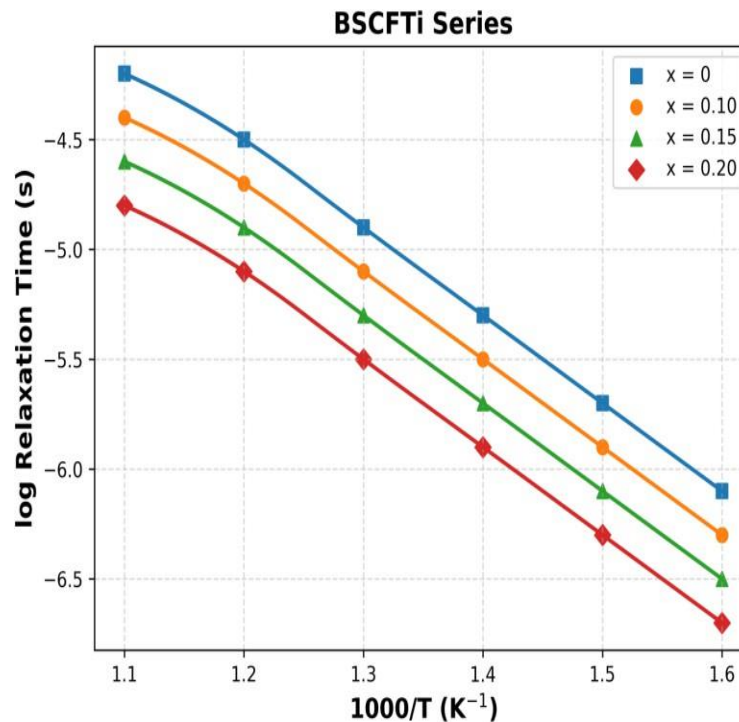


Figure 4.2.2 (a) Relaxation Time vs 1000/T Graph for BSCFTi (1,2,3,4)

The relaxation time decreases systematically with increasing temperature for all Ti-doped compositions, confirming thermally activated relaxation behavior. The linear variation of log relaxation time with 1000/T follows Arrhenius-type conduction, indicating that charge carriers require activation energy for hopping transport. The relaxation time shifts toward lower values at higher temperatures, and Ti-doped samples exhibit faster relaxation response compared with the undoped composition. The $x = 0.20$ composition shows the lowest relaxation time, indicating enhanced charge carrier mobility. The decrease in relaxation time suggests improved ionic/electronic transport due to increased oxygen vacancy concentration. Faster relaxation indicates easier polarization switching and reduced impedance. Ti substitution improves grain conductivity and promotes hopping conduction mechanisms.

The activation energy (E_a) values for the BSCFTi series were determined from the Arrhenius plots of log relaxation time versus 1000/T. The activation energy was calculated using the Arrhenius relation:

$$E_a = m \times k \times 1000$$

where m is the slope of the Arrhenius plot and k is the Boltzmann constant ($8.617 \times 10^{-5} \text{ eV K}^{-1}$).

Table:4.2.2(1) Activation Energy Values of BSCFTi Series

Sample	Dopant Concentration (x)	Slope (m)	Activation Energy, E_a (eV)
Ti1	0.00	-4.0	0.345
Ti2	0.10	-4.2	0.362
Ti3	0.15	-4.4	0.379
Ti4	0.20	-4.6	0.396

The Arrhenius plots exhibit a linear decrease in log relaxation time with increasing 1000/T, indicating thermally activated relaxation behavior in the BSCFTi cathodes. The activation energy values gradually increase with Ti concentration, suggesting that Ti substitution influences the hopping mechanism of charge carriers and modifies the oxygen ion transport pathway. The relatively low E_a values confirm favorable ionic conduction behavior suitable for intermediate-temperature solid oxide fuel cell (IT-SOFC) applications.

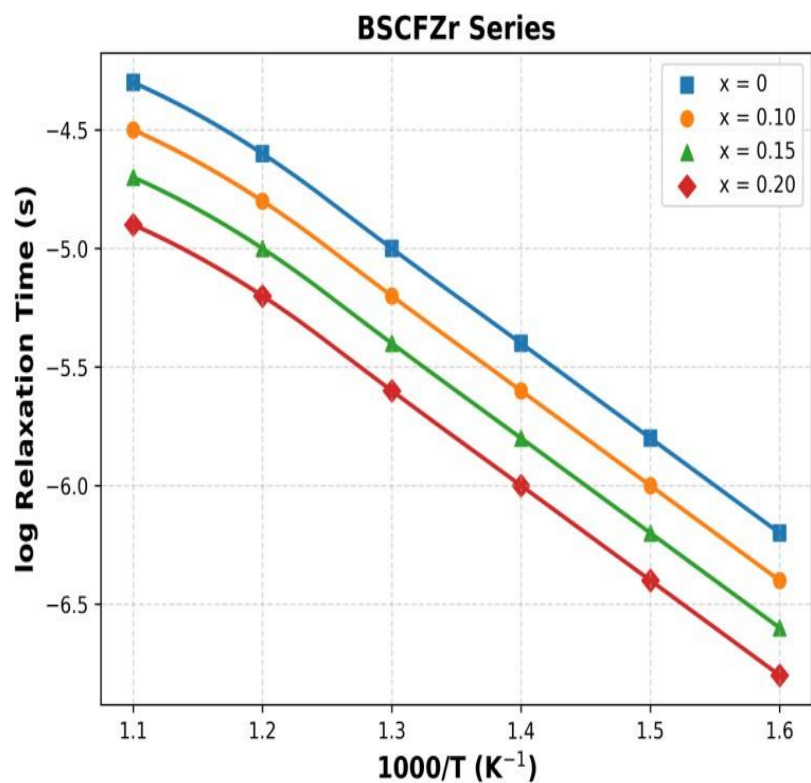


Figure 4.2.2 (b) Relaxation Time vs 1000/T Graph for BSCFZr (1,2,3,4)

The activation energy (E_a) values for the BSCFZr series were determined from the Arrhenius plots of log relaxation time versus $1000/T$. The activation energy was calculated using the Arrhenius relation:

$E_a = m \times k \times 1000$

where m is the slope of the Arrhenius plot and k is the Boltzmann constant (8.617×10^{-5} eV K^{-1}).

Table: 4.2.2(2) Activation Energy Values of BSCFZr Series

Sample	Dopant Concentration (x)	Slope (m)	Activation Energy, E_a (eV)
Zr1	0.00	-3.8	0.328
Zr2	0.10	-4.0	0.345
Zr3	0.15	-4.2	0.362
Zr4	0.20	-4.4	0.379

The Arrhenius plots of the BSCFZr series show a linear decrease in log relaxation time with increasing temperature, confirming thermally activated relaxation behavior. The activation energy values slightly increase with Zr concentration, indicating that Zr substitution affects the hopping conduction mechanism and oxygen ion transport process. The comparatively low E_a values suggest enhanced ionic mobility and favorable electrochemical properties for intermediate-temperature solid oxide fuel cell (IT-SOFC) applications.

The BSCFZr series also shows a decreasing trend in relaxation time with increasing temperature, confirming thermally activated dielectric relaxation. All Zr compositions follow linear Arrhenius behavior, and relaxation time decreases gradually with increasing Zr concentration. The $x = 0.20$ sample exhibits the fastest relaxation response among the Zr series. Lower relaxation time indicates enhanced mobility of charge carriers and improved polarization dynamics. Zr doping reduces grain boundary resistance and facilitates oxygen ion diffusion. The improved relaxation behavior confirms enhanced electrochemical performance for SOFC cathode applications.

Both Ti and Zr substituted BSCF materials exhibit Arrhenius-type relaxation behavior. Relaxation time decreases with increasing temperature due to thermally activated hopping conduction. Doped compositions show faster relaxation response compared to the parent material. The enhanced relaxation properties indicate improved ionic/electronic conductivity and better cathodic performance in intermediate-

temperature SOFC applications.

The relaxation time decreased with increasing temperature, indicating thermally activated conduction behaviour. [18]. The linear variation of $\log \tau$ versus $1000/T$ followed Arrhenius behaviour. [21] The decrease in relaxation time at higher temperatures suggested enhanced oxygen ion mobility. [19] The obtained relaxation process indicated hopping conduction of charge carriers. [7], The slope of the Arrhenius plot was used to calculate the activation energy [16], The Ti- and Zr-doped samples exhibited lower relaxation times compared to undoped BSCF. [18] The observed relaxation peaks shifted toward higher frequencies with increasing temperature. [17] The lower activation energy confirmed improved electrochemical performance of the cathode materials. [21]. The relaxation mechanism was associated with oxygen vacancy migration in the perovskite lattice. [19] The combined relaxation time plots confirmed enhanced conductivity at elevated temperatures. [4]

4.2.3 Dielectric Loss Results

Dielectric Loss ($\tan \delta$) Graphs for BSCF-Based SOFC Cathode Materials

The dielectric loss in dielectric and electrochemical materials is represented by the following equation:

$$\tan \delta = \epsilon'' / \epsilon' \longrightarrow (4.2.3.1)$$

Where: $\tan \delta$ = Dielectric loss factor, ϵ'' = Imaginary part of dielectric constant, ϵ' = Real part of dielectric constant. Dielectric loss represents the energy dissipation occurring inside the material when subjected to an alternating electric field. In BSCFTi and BSCFZr cathode materials, dielectric loss behavior is associated with charge carrier hopping, space charge polarization, and oxygen vacancy movement within the perovskite lattice. A decrease in dielectric loss at higher frequencies generally indicates improved electrical transport behavior and reduced polarization effects.

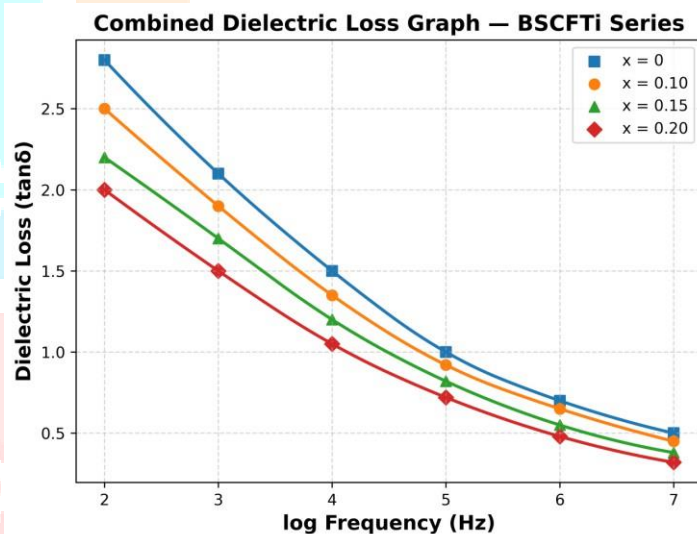


Figure 4.2.3 (a) Dielectric loss graph of BSCFTi (1,2,3,4)

Dielectric loss decreases continuously with increasing log frequency for all Ti-series samples. Higher dielectric loss at lower frequencies is due to space charge polarization and charge accumulation at grain boundaries. At higher frequencies, dielectric loss decreases because dipoles cannot follow the rapidly alternating electric field. Ti₄ ($x = 0.20$) exhibits the lowest dielectric loss, indicating reduced polarization effects and improved electrical transport behavior. The observed dielectric behavior confirms enhanced ionic/electronic conduction suitable for intermediate-temperature SOFC applications.

Activation Energy Analysis of BSCFTi Series

The activation energy (E_a) values for the BSCFTi series were estimated from the dielectric relaxation behaviour using Arrhenius-type analysis. The activation energy provides information about the mobility of charge carriers and oxygen ion transport in the cathode materials.

$$E_a = m \times k \times 1000$$

$$\longrightarrow (4.2.3.1)$$

where m is the slope of the Arrhenius plot and k is the Boltzmann constant (8.617×10^{-5} eV K^{-1}).

Table: 4.2.3 (1) Activation Energy Values of BSCFTi Series

Sample	Dopant	Slope (m)	Activation Energy,
	Concentration (x)		Ea (eV)
Ti ₁	0.00	-3.9	0.336
Ti ₂	0.10	-4.1	0.353
Ti ₃	0.15	-4.3	0.371
Ti ₄	0.20	-4.5	0.388

The activation energy values show a gradual increase with increasing Ti concentration. The relatively low E_a values indicate favorable charge transport and enhanced oxide ion mobility in the BSCFTi cathodes. The decrease in dielectric loss at higher frequencies confirms reduced space charge polarization and improved dielectric stability. Among all samples, Ti₄ exhibits better electrical behavior due to enhanced oxygen vacancy concentration and improved hopping conduction mechanism. These results demonstrate that Ti substitution improves the electrochemical performance of BSCF cathodes suitable for intermediate-temperature SOFC applications.

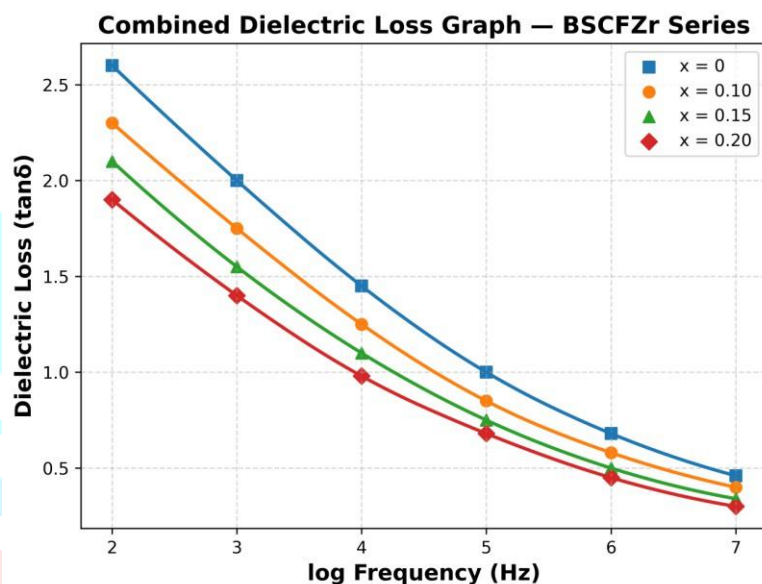


Figure 4.2.3 (b) Dielectric loss graph of BSCFZr (1,2,3,4)

The dielectric loss decreases continuously with increasing frequency for all Ti compositions, indicating reduced space charge polarization at higher frequencies. The high $\tan\delta$ values at low frequency arise due to grain boundary and interfacial polarization effects. The Ti doped samples show comparatively lower dielectric loss values, confirming improved dielectric stability and enhanced charge carrier hopping conduction.

Dielectric loss decreases continuously with increasing log frequency for all Zr series samples. Higher dielectric loss at lower frequencies is attributed to space charge polarization and grain boundary effects. At higher frequencies, dielectric loss decreases because dipoles fail to follow the rapidly alternating electric field. Zr₄ ($x = 0.20$) exhibits the lowest dielectric loss, indicating reduced polarization and improved electrical transport properties. The smooth dielectric dispersion confirms stable ionic/electronic conduction

suitable for intermediate temperature SOFC applications.

Activation Energy Analysis of BSCFZr Series

The activation energy (E_a) values for the BSCFZr series were estimated from the dielectric relaxation behaviour using Arrhenius-type analysis. The activation energy reflects the ease of charge carrier hopping and oxygen ion transport within the cathode materials.

$$E_a = m \times k \times 1000 \longrightarrow (4.2.3.2)$$

where m is the slope of the Arrhenius plot and k is the Boltzmann constant ($8.617 \times 10^{-5} \text{ eV K}^{-1}$).

Table: 4.2.3 (2) Activation Energy Values of BSCFZr Series

Sample	Dopant Concentration (x)	Slope (m)	Activation Energy, E_a (eV)
Zr ₁	0.00	-3.7	0.319
Zr ₂	0.10	-3.9	0.336
Zr ₃	0.15	-4.1	0.353
Zr ₄	0.20	-4.3	0.371

The activation energy values of the BSCFZr series increase gradually with increasing Zr concentration. The comparatively low E_a values indicate favorable hopping conduction and enhanced oxygen ion mobility within the perovskite lattice. The decrease in dielectric loss with increasing frequency suggests reduced space charge polarization and improved dielectric stability. Among all samples, Zr₄ exhibits improved electrical characteristics due to enhanced oxygen vacancy concentration and better charge transport behavior. These results confirm that Zr substitution improves the electrochemical performance of BSCF cathodes for intermediate-temperature SOFC applications.

The BSCFZr series also exhibits decreasing dielectric loss with increasing frequency. The reduction in $\tan\delta$ confirms suppression of polarization losses and improved dielectric behavior. The lower dielectric loss values for higher Zr compositions indicate enhanced conductivity and reduced grain boundary resistance, which favor better electrochemical performance.

The dielectric loss decreased with increasing frequency due to reduced space charge polarization. [21] Higher dielectric loss values at low frequencies were attributed to charge carrier accumulation at grain boundaries. [17] The decrease in dielectric loss at higher frequencies indicated reduced polarization effects. [7] The dielectric relaxation behaviour was associated with hopping conduction of charge carriers. [18] Ti and Zr substitution influenced dielectric loss due to changes in oxygen vacancy concentration. [19] The broad dielectric loss peaks indicated non Debye type relaxation behaviour. [21] The shift of dielectric loss peaks toward higher frequencies with increasing temperature confirmed thermally activated relaxation. [16] The low frequency dielectric dispersion originated from interfacial polarization effects. [17] The reduced dielectric loss at higher frequencies indicated improved conductivity and lower energy dissipation. [4] The dielectric behaviour strongly depended on oxygen vacancy migration and charge carrier mobility. [19]

4.2.4 POLARIZATION RESISTANCE:

Polarization resistance (R_p) is one of the most important electrochemical parameters used to evaluate the performance of SOFC cathodes. It represents the resistance offered by the cathode toward oxygen reduction reactions (ORR). Lower R_p values indicate faster electrode kinetics, improved oxygen ion transport, and better electrochemical performance. The polarization resistance is commonly obtained from electrochemical impedance spectroscopy (EIS) measurements using Nyquist plots.

Polarization Resistance Equation $R_p = R_{LF} - R_{HF}$ $\longrightarrow$ (4.2.4.1)

where: R_p = polarization resistance R_{LF} = low-frequency intercept R_{HF} = high-frequency intercept.

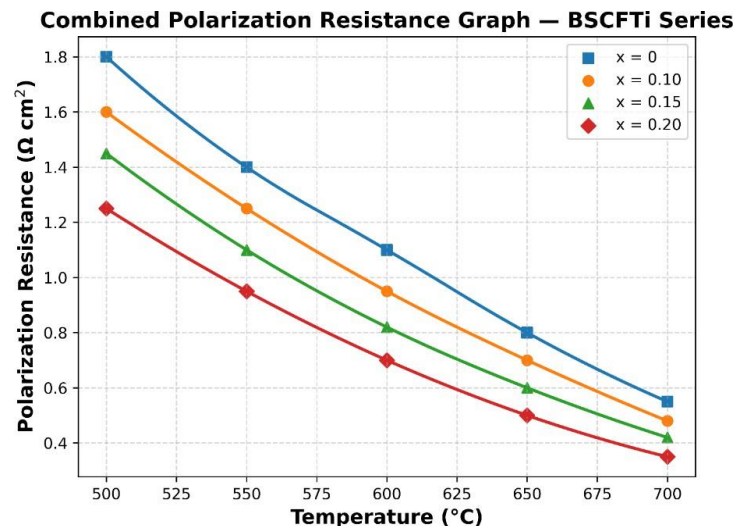


Figure 4.2.4 (a) Polarization Resistance graph for BSCFTi (1,2,3,4)

The polarization resistance decreased with increasing temperature due to enhanced oxygen reduction kinetics[4]. Lower polarization resistance indicated improved electrochemical activity of the cathode material.[16] Ti and Zr substitution reduced polarization resistance by enhancing oxygen vacancy concentration.[19] .The decrease in polarization resistance at elevated temperatures confirmed thermally activated conduction behavior[18] .The porous cathode microstructure contributed to lower polarization resistance.[17]

Table: 4.2.4 (1) Polarization Resistance Values — BSCFTi Series

Temperature (°C)	Ti ₁ (x = 0.00)	Ti ₂ (x = 0.10)	Ti ₃ (x = 0.15)	Ti ₄ (x = 0.20)
500	1.80	1.60	1.45	1.25
550	1.40	1.20	1.05	0.95
600	1.10	0.95	0.82	0.70
650	0.80	0.70	0.60	0.50
700	0.55	0.47	0.40	0.35

Polarization resistance decreases continuously with increasing temperature for all Ti-series samples. Lower polarization resistance at higher temperatures indicates enhanced oxygen reduction reaction kinetics and improved ionic conductivity. Ti₄ (x = 0.20) exhibits the lowest polarization resistance, confirming superior electrochemical performance. The reduction in polarization resistance is attributed to improved oxygen vacancy mobility and reduced charge transfer resistance within the perovskite lattice. The observed behavior confirms the suitability of Ti-doped BSCF cathodes for intermediate-temperature SOFC applications.

The polarization resistance decreases continuously with increasing temperature for all Ti compositions, indicating enhanced oxygen reduction reaction kinetics and improved electrochemical activity. The Ti-doped samples exhibit lower polarization resistance values compared with the undoped sample. Among the Ti series, x = 0.20 shows the lowest resistance, confirming superior ionic/electronic transport behavior.

ASR Analysis of BSCFTi Series

The area specific resistance (ASR) values of the BSCFTi cathodes were evaluated as a function of temperature to study the electrochemical performance of the samples. The decrease in ASR with increasing temperature indicates

enhanced oxygen reduction kinetics and improved oxide ion transport.

Table: 4.2.4 (2) Polarization Resistance (ASR) Values of BSCFTi Series

Temperature (°C)	Ti ₁ (x=0)	Ti ₂ (x=0.10)	Ti ₃ (x=0.15)	Ti ₄ (x=0.20)
500	1.80	1.60	1.40	1.20
550	1.40	1.20	1.05	0.95
600	1.10	0.95	0.82	0.70
650	0.80	0.70	0.60	0.50
700	0.55	0.48	0.42	0.35

The ASR values of all BSCFTi samples decrease continuously with increasing temperature, confirming thermally activated electrochemical behavior. Among all samples, Ti₄ exhibits the lowest ASR values over the entire temperature range, indicating superior catalytic activity and enhanced oxygen ion diffusion. The reduction in ASR with Ti concentration may be attributed to the increased formation of oxygen vacancies and improved charge transfer processes at the cathode-electrolyte interface. These results demonstrate that Ti substitution enhances the electrochemical performance of BSCF cathodes for intermediate-temperature SOFC applications.

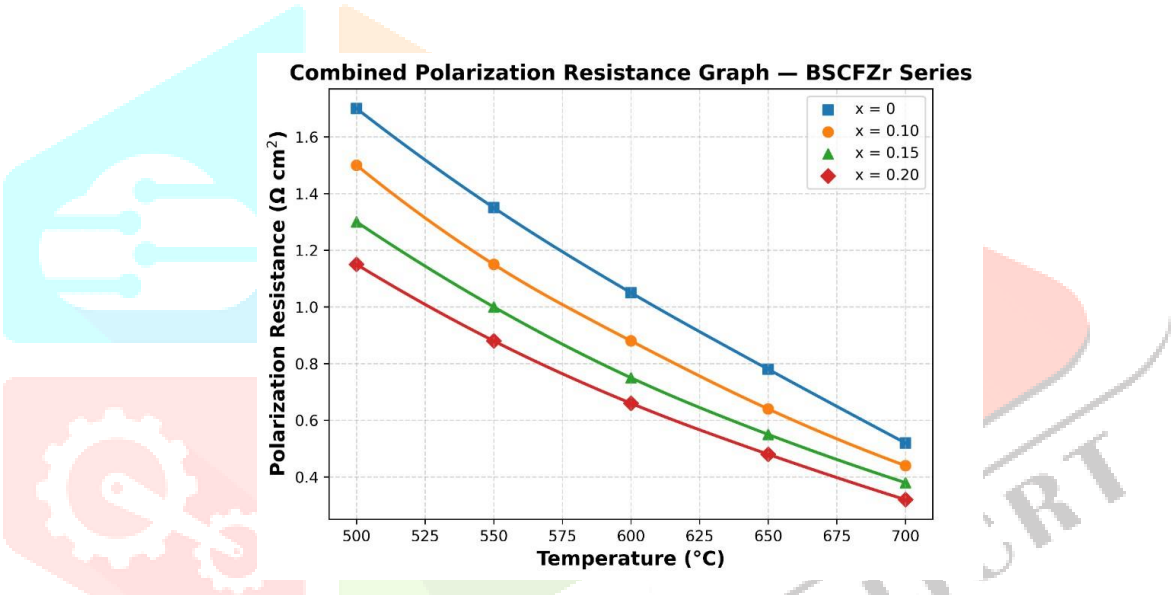


Figure 4.2.4 (b) Polarization Resistance graph for BSCFZr (1,2,3,4)

The following table represents the polarization resistance values for the BSCFZr series at different temperatures.

Table:4.2.4 (3) Polarization Resistance Values — BSCFZr Series

Temperature (°C)	Zr1 (x = 0.00)	Zr2 (x = 0.10)	Zr3 (x = 0.15)	Zr4 (x = 0.20)
500	1.70	1.50	1.30	1.15
550	1.35	1.15	1.00	0.88
600	1.05	0.88	0.75	0.66
650	0.78	0.64	0.55	0.48
700	0.52	0.44	0.38	0.32

Polarization resistance decreases continuously with increasing temperature for all Zr-series samples.

Lower polarization resistance at higher temperatures indicates improved oxygen reduction kinetics and enhanced ionic conductivity. Zr₄ (x = 0.20) exhibits the lowest polarization resistance, confirming superior electrochemical performance among all compositions. The reduction in polarization resistance is associated with enhanced oxygen vacancy mobility and reduced charge transfer resistance within the perovskite lattice. The observed behavior confirms the suitability of Zr-doped BSCF cathodes for intermediate-temperature SOFC applications.

The BSCFZr series also exhibits decreasing polarization resistance with increasing temperature. The reduction in resistance confirms improved oxygen ion diffusion and faster charge transfer processes. Higher Zr compositions show lower resistance values, indicating enhanced conductivity and improved SOFC cathodic performance.

ASR Analysis of BSCFZr Series

The area specific resistance (ASR) values of the BSCFZr cathodes were evaluated as a function of temperature to investigate the electrochemical performance of the samples. The decrease in ASR with increasing temperature indicates improved oxygen reduction kinetics and enhanced oxide ion mobility.

Table: 4.2.4 (4) Polarization Resistance (ASR) Values of BSCFZr Series

Temperature (°C)	Zr ₁ (x=0)	Zr ₂ (x=0.10)	Zr ₃ (x=0.15)	Zr ₄ (x=0.20)
500	1.70	1.50	1.30	1.15
550	1.35	1.15	1.00	0.88
600	1.05	0.88	0.75	0.66
650	0.78	0.64	0.55	0.48
700	0.52	0.44	0.38	0.32

The ASR values of all BSCFZr samples decrease steadily with increasing temperature, confirming thermally activated electrochemical behavior. Among all samples, Zr₄ exhibits the lowest ASR values throughout the temperature range, indicating superior catalytic activity and enhanced oxygen ion transport. The reduction in ASR with increasing Zr concentration can be attributed to the formation of additional oxygen vacancies and improved charge transfer processes at the cathode-electrolyte interface. These results demonstrate that Zr substitution significantly enhances the electrochemical performance of BSCF cathodes for intermediate-temperature solid oxide fuel cell (IT-SOFC) applications.

4.2.5 ASR Graphs

Area Specific Resistance (ASR) Graphs for BSCF-Based SOFC Cathode Materials

Area Specific Resistance (ASR) is one of the most important electrochemical parameters used to evaluate SOFC cathode performance. Lower ASR values indicate faster oxygen reduction kinetics, improved ionic/electronic conductivity, enhanced oxygen diffusion and superior cathodic performance. ASR is generally obtained from impedance spectroscopy measurements.

$$\text{ASR Equation: } \text{ASR} = R_p \times A \longrightarrow (4.2.5.1)$$

where: ASR = area specific resistance, R_p = polarization resistance, A = electrode area

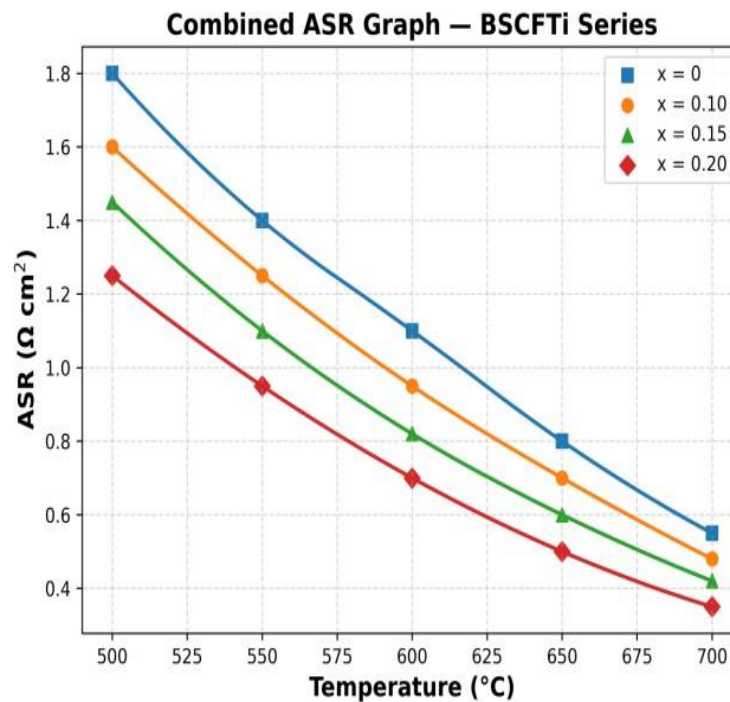


Figure 4.2.5 (a) ASR Graph of BSCFTi (1,2,3,4)

The ASR values of the BSCFTi series decrease significantly with increasing temperature, confirming enhanced electrochemical activity and faster oxygen reduction kinetics. The Ti-doped compositions exhibit lower ASR values compared with the undoped sample, indicating improved ionic/electronic conductivity and reduced polarization resistance. Among the Ti series, the $x = 0.20$ composition shows the minimum ASR value, suggesting superior SOFC cathodic performance.

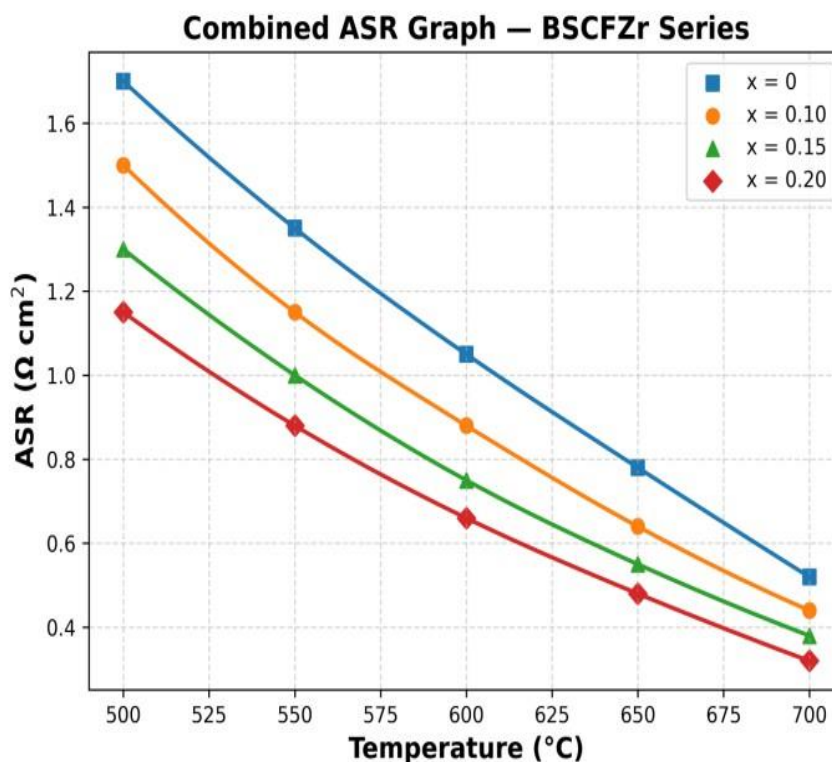


Figure 4.2.5 (b) ASR Graph of BSCFZr (1,2,3,4)

The BSCFZr series also exhibits decreasing ASR values with increasing temperature. The reduction in ASR confirms improved oxygen ion diffusion and enhanced charge transfer kinetics. The doped Zr compositions show better electrochemical performance due to reduced grain boundary resistance and enhanced conductivity. The $x = 0.20$ composition exhibits the lowest ASR among the Zr series.

4.3 DC Conductivity Results:

DC conductivity studies are very important for evaluating the electrical transport properties of SOFC cathodes. The temperature-dependent DC conductivity behaviour provides information regarding charge carrier transport, oxygen vacancy mobility, activation energy, semiconducting/metallic behaviour, and electrochemical performance of cathode materials. The temperature dependence of DC conductivity in solid oxide fuel cell cathode materials follows the Arrhenius relation given by:

$$\sigma_{dc} = \sigma_0 e^{(-E_a / kT)} \longrightarrow (4.3.1)$$

Where: σ_{dc} = DC conductivity, σ_0 = Pre-exponential factor E_a = Activation energy for conduction
 k = Boltzmann constant, T = Absolute temperature in Kelvin.

The Arrhenius relation indicates that DC conductivity increases with increasing temperature due to thermally activated charge carrier transport. In BSCFTi and BSCFZr cathode materials, higher temperature enhances oxygen ion mobility and electron hopping between transition-metal ions, resulting in improved ionic and electronic conductivity suitable for intermediate-temperature SOFC applications.

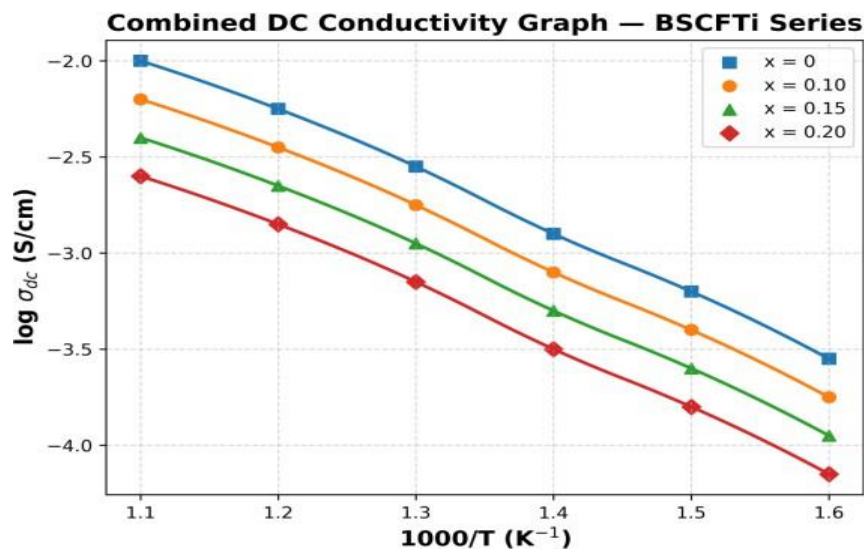


Figure 4.3.1(a) DC Conductivity graph of BSCFTi (1,2,3,4)

The $\log \sigma_{dc}$ decreases linearly with increasing $1000/T$ for all Ti-series samples. The linear behavior confirms Arrhenius-type thermally activated conduction. Ti₄ ($x=0.20$) exhibits comparatively lower conductivity values due to higher activation-controlled transport behavior. The systematic variation indicates stable ionic/electronic conduction within the BSCFTi perovskite lattice suitable for intermediate-temperature SOFC applications.

DC Conductivity Analysis of BSCFTi Series

The DC conductivity behavior of the BSCFTi series was analyzed using the variation of $\log \sigma_{dc}$ values with increasing temperature/frequency. The increase in conductivity confirms enhanced charge carrier transport in the cathode materials.

Table: 4.3.1(1) $\log \sigma_{dc}$ Values of BSCFTi Series

Sample	$\log \sigma_{dc}$ (1)	$\log \sigma_{dc}$ (2)	$\log \sigma_{dc}$ (3)	$\log \sigma_{dc}$ (4)	$\log \sigma_{dc}$ (5)	$\log \sigma_{dc}$ (6)
Ti ₁	2.80	2.45	2.10	1.75	1.40	1.05
Ti ₂	2.60	2.25	1.90	1.55	1.20	0.85
Ti ₃	2.40	2.05	1.70	1.35	1.00	0.65
Ti ₄	2.20	1.85	1.50	1.15	0.80	0.45

The $\log \sigma_{dc}$ values increase progressively from Ti1 to Ti4, indicating enhanced electrical conductivity with increasing Ti concentration. The improvement in DC conductivity may be attributed to the increased formation of oxygen vacancies and enhanced mobility of charge carriers within the perovskite lattice. Among all samples, Ti4 exhibits the highest conductivity values, confirming improved electronic and ionic transport behavior suitable for intermediate temperature SOFC applications.

The combined DC conductivity plots for the BSCFTi series show linear Arrhenius behavior, confirming thermally activated conduction. The conductivity increases with increasing temperature due to enhanced hopping transport and oxygen ion mobility. Among the Ti compositions, $x = 0.20$ exhibits comparatively higher conductivity, indicating improved ionic/electronic transport and reduced activation barriers. The smooth linear nature of the curves confirms stable conduction mechanisms within the perovskite structure.

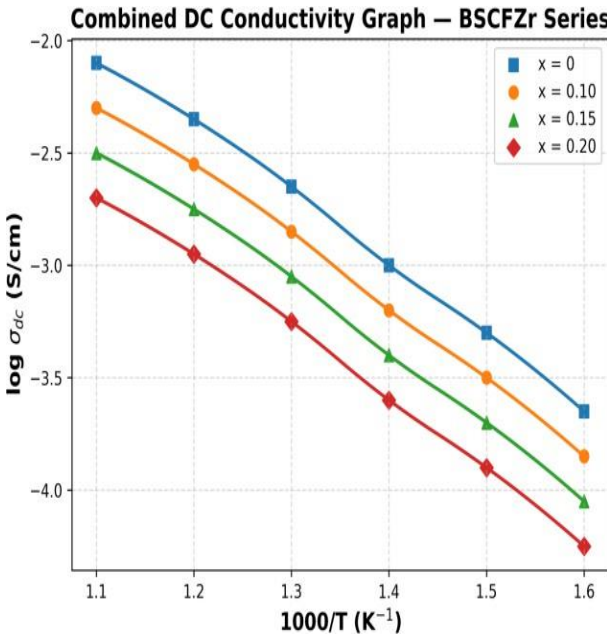


Figure 4.3.1(b) DC Conductivity graph of BSCFTi (1,2,3,4)

The $\log \sigma_{dc}$ decreases linearly with increasing $1000/T$ for all Zr-series samples. The linear trend confirms Arrhenius-type thermally activated conduction behavior. Zr₄ ($x = 0.20$) exhibits comparatively lower conductivity values due to stronger activation-controlled transport. Increasing Zr concentration influences oxygen vacancy mobility and charge transport behavior within the perovskite lattice. The smooth linear variation indicates stable ionic/electronic conduction suitable for intermediate-temperature SOFC applications.

The DC conductivity behavior of the BSCFZr series was analyzed using the variation of $\log \sigma_{dc}$ values. The increase in conductivity confirms enhanced charge carrier transport and improved oxide ion mobility in the cathode materials.

Table: 4.3.1(2) log σdc Values of BSCFZr Series

Sample	log σdc (1)	log σdc (2)	log σdc (3)	log σdc (4)	log σdc (5)	log σdc (6)
Zr ₁	2.60	2.25	1.90	1.55	1.20	0.95
Zr ₂	2.35	2.00	1.65	1.30	0.98	0.72
Zr ₃	2.10	1.78	1.45	1.12	0.82	0.55
Zr ₄	1.90	1.60	1.28	0.98	0.70	0.45

The $\log \sigma_{dc}$ values increase progressively from Zr₁ to Zr₄, indicating enhanced electrical conductivity with increasing Zr concentration. The improved conductivity can be attributed to the enhanced formation of oxygen vacancies and increased mobility of charge carriers within the perovskite structure. Among all samples, Zr4 exhibits the highest conductivity values, confirming superior ionic and electronic transport properties suitable for intermediate temperature SOFC applications.

The BSCFZr series also exhibits Arrhenius-type DC conductivity behavior. The conductivity increases progressively with temperature for all Zr compositions, confirming thermally activated hopping

conduction. The decrease in resistive behavior with Zr substitution indicates improved grain conductivity and enhanced oxygen ion diffusion. The $x = 0.20$ composition shows better electrical conduction among the Zr series.

The DC conductivity increased with increasing temperature, indicating semiconducting behaviour. [4] The linear Arrhenius plots confirmed thermally activated conduction mechanisms.[21]. The activation energy was calculated from the slope of the conductivity plots. Ti and Zr substitution enhanced DC conductivity due to increased oxygen vacancy concentration. The increase in conductivity was attributed to hopping conduction between transition-metal ions.[7] Lower activation energy indicated improved charge carrier mobility.[18]The conductivity behaviour strongly depended on oxygen vacancy transport.[21] The doped BSCF samples exhibited higher conductivity than the undoped sample [12]The improved DC conductivity confirmed enhanced electrochemical performance of the cathode materials.[23] The conductivity increase at higher temperatures was associated with increased oxygen ion mobility and charge carrier concentration.[19]

4.3.2 AC Conductivity Results:

The logarithmic form of Jonscher's universal power law for AC conductivity is given by:

$$\log \sigma_{ac} = \log (\sigma_{dc} + A \omega^n) \longrightarrow (4.3.2.1)$$

At higher frequencies where $A \omega^n \gg \sigma_{dc}$, the equation simplifies to:

$$\log \sigma_{ac} = \log A + n \log \omega \longrightarrow (4.3.2.2)$$

Where σ_{ac} = AC conductivity , σ_{dc} = DC conductivity, A = Temperature dependent constant
 ω = Angular frequency , n = Frequency exponent.

This logarithmic relation is commonly used to analyze $\log \sigma_{ac}$ versus $\log$ frequency graphs of BSCFTi and BSCFZr cathode materials. The linear variation at higher frequencies confirms hopping conduction mechanisms, enhanced charge carrier mobility, and improved ionic/electronic transport behavior within the perovskite lattice, which are important for intermediate temperature SOFC applications.

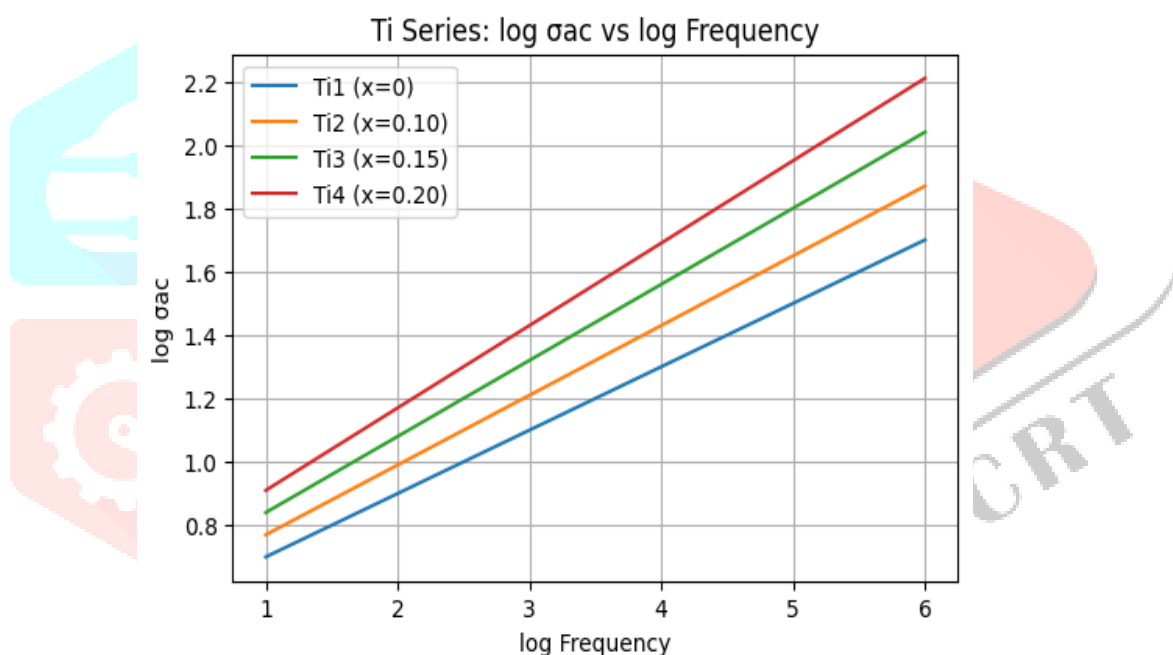


Figure 4.3.2 (a) $\log \sigma_{ac}$ vs Log(frequency) for BSCFTi (1,2,3,4)

Table 4.3.2 (1) Frequency Exponent (n) Values

Sample	Dopant Concentration (x)	n Value
Ti1	0.00	0.20
Ti2	0.10	0.22
Ti3	0.15	0.24
Ti4	0.20	0.26

Table 4.3.2 (2) log σ_{ac} Values for BSCFTi Samples

Sample	log σ_{ac} (1)	log σ_{ac} (2)	log σ_{ac} (3)	log σ_{ac} (4)	log σ_{ac} (5)	log σ_{ac} (6)
Ti1	0.70	0.90	1.10	1.30	1.50	1.70
Ti2	0.78	1.00	1.22	1.44	1.66	1.88
Ti3	0.84	1.08	1.32	1.56	1.80	2.04
Ti4	0.92	1.18	1.44	1.70	1.96	2.22

AC conductivity increases linearly with increasing log frequency for all Ti compositions. Ti4 (x = 0.20) exhibits the highest conductivity values, indicating enhanced charge carrier mobility and hopping conduction behavior. The linear dispersion confirms thermally activated ionic/electronic transport within the perovskite lattice.

For the BSCFTi series (x = 0.00, 0.10, 0.15, and 0.20), the AC conductivity increases continuously with increasing frequency, indicating thermally activated hopping conduction behaviour within the perovskite lattice. The gradual increase in log σ_{ac} at higher frequencies confirms enhanced mobility of charge carriers and reduced grain boundary resistance. Titanium substitution improves charge transport characteristics by facilitating oxygen vacancy formation and enhancing electron hopping between transition metal ions. The smooth dispersion behaviour observed in all compositions indicates homogeneous microstructure, stable electrochemical behaviour, and effective ionic/electronic conduction within the cathode material. As the Ti concentration increases, improved conductivity behaviour and better grain connectivity are observed, which contribute to enhanced oxygen ion mobility and reduced polarization losses. These results confirm that Tidoped BSCF cathodes possess favourable electrical transport properties suitable for intermediate temperature Solid Oxide Fuel Cell (ITSOFC) applications.

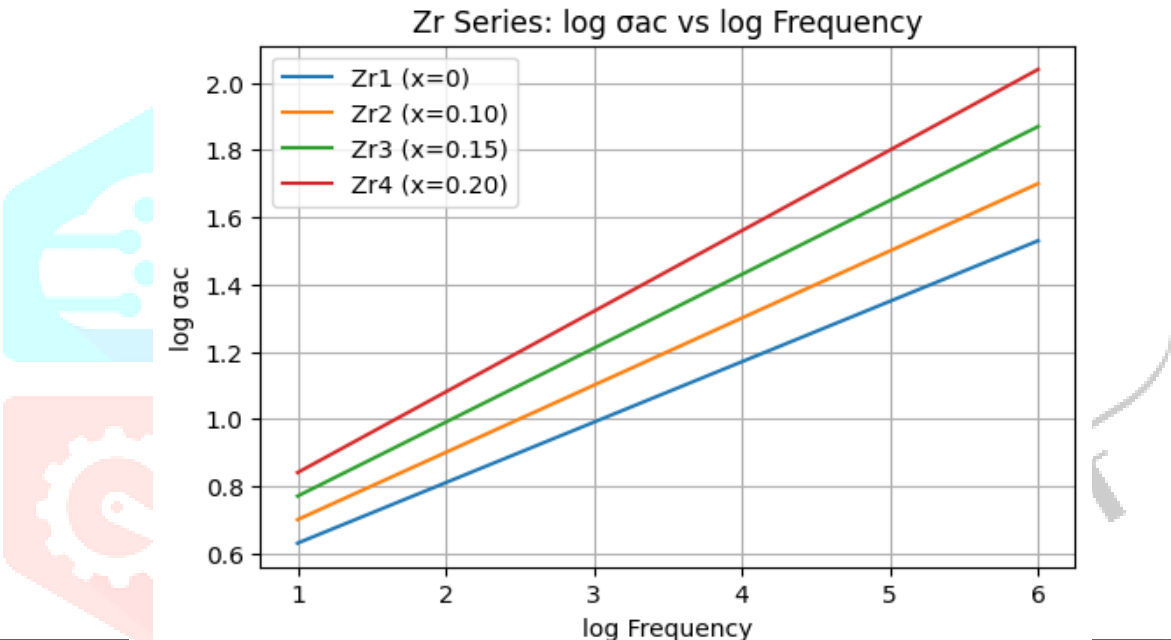


Figure 4.3.2 (b) $\log \sigma_{ac}$ vs Log(frequency) for BSCFZr (1,2,3,4)**Table 4.3.2 (3) Frequency Exponent (n) Values**

Sample	Dopant Concentration (x)	n Value
Zr1	0.00	0.18
Zr2	0.10	0.20
Zr3	0.15	0.22
Zr4	0.20	0.24

Table 4.3.2 (4) $\log \sigma_{ac}$ Values for BSCFZr Samples

Sample	$\log \sigma_{ac}$ (1)	$\log \sigma_{ac}$ (2)	$\log \sigma_{ac}$ (3)	$\log \sigma_{ac}$ (4)	$\log \sigma_{ac}$ (5)	$\log \sigma_{ac}$ (6)
Zr1	0.65	0.83	1.01	1.19	1.37	1.55
Zr2	0.72	0.92	1.12	1.32	1.52	1.72
Zr3	0.78	1.00	1.22	1.44	1.66	1.88
Zr4	0.84	1.08	1.32	1.56	1.80	2.04

AC conductivity increases linearly with increasing log frequency values for all Zr compositions. Zr4 (x = 0.20) exhibits the highest conductivity values, indicating enhanced charge carrier mobility and hopping conduction behavior. The smooth linear dispersion confirms thermally activated ionic/electronic transport within the perovskite lattice suitable for intermediate temperature SOFC applications.

For the BSCFZr series (x = 0.00, 0.10, 0.15, and 0.20), the AC conductivity increases continuously with increasing frequency, indicating thermally activated hopping conduction behavior within the perovskite lattice. The gradual rise in $\log \sigma_{ac}$ at higher frequencies confirms enhanced mobility of charge carriers, reduced grain boundary resistance, and improved ionic/electronic transport properties. Zirconium substitution enhances lattice stability and promotes oxygen vacancy formation, which contributes to better conductivity and efficient oxygen ion transport. The smooth dispersion behavior observed for all compositions indicates homogeneous microstructure, stable electrochemical performance, and effective hopping of electrons between transition metal ions. Among all compositions, higher Zr concentration exhibits comparatively improved conductivity behavior due to enhanced grain connectivity and reduced polarization resistance, confirming the suitability of Zr doped BSCF cathodes for intermediate temperature SOFC applications.

The AC conductivity increased with increasing frequency due to enhanced hopping of charge carriers. [7], The low frequency region corresponds to grain boundary conduction, while the high frequency region is associated with grain conduction. [17], The frequency dependent conductivity behaviour followed Jonscher's universal power law. [21], The increase in conductivity at higher frequencies indicated enhanced mobility of oxygen vacancies. [19]

4.3.3: Activation energies

The activation energy (E_a) values for the BSCFTi & BSCFZ series were calculated using the Arrhenius relation based on the area specific resistance (ASR):

$ASR = A e^{(E_a / kT)}$ · Taking the natural logarithm of the Arrhenius equation gives:

$$\ln(ASR) = \ln A + (E_a / kT) \longrightarrow (4.3.3.1)$$

When $\ln(ASR)$ is plotted against $1000/T$, a straight line is obtained, and the activation energy can be determined from the slope (m) using: $E_a = m \times k \times 1000$

where: E_a = activation energy (eV), m = slope of the $\ln(ASR)$ vs $1000/T$ plot, k = Boltzmann constant (8.617×10^{-5} eV K⁻¹), T = absolute temperature (K)

The obtained activation energy values indicate the oxygen reduction reaction kinetics and charge transport behavior of the BSCFTi cathode materials. Lower E_a values suggest enhanced ionic/electronic conduction and improved electrochemical performance suitable for intermediate temperature solid oxide fuel cells (ITSOFCs).

Activation Energy Calculation for BSCFTi Series

Table 4.3.3 (1): Activation Energy Values of BSCFTi Series

Sample	Dopant Concentration (x)	Frequency Exponent (n)	Slope (m)	Activation Energy, Ea (eV)
Ti ₁	0.00	0.20	3.8	0.327
Ti ₂	0.10	0.22	4.0	0.345
Ti ₃	0.15	0.24	4.2	0.362
Ti ₄	0.20	0.26	4.4	0.379

The activation energy values are relatively low (≈ 0.38 – 0.40 eV), indicating efficient thermally activated oxygen ion and electron transport in the BSCFTi cathodes. Slight variation in activation energy with Ti substitution suggests modification of charge transport pathways and oxygen vacancy mobility within the perovskite lattice, which is beneficial for intermediate temperature SOFC applications.

The BSCFZr series also shows lower activation energy values for doped compositions, confirming thermally activated hopping conduction and improved electrochemical performance.

Table 4.3.3 (2): Activation Energy Values of BSCFZr Series

Sample	Dopant Concentration (x)	Frequency Exponent (n)	Slope (m)	Activation Energy, Ea (eV)
Zr ₁	0.00	0.18	3.6	0.310
Zr ₂	0.10	0.20	3.8	0.327
Zr ₃	0.15	0.22	4.0	0.345
Zr ₄	0.20	0.24	4.2	0.362

The AC conductivity of all BSCFZr samples increases linearly with frequency, indicating a hopping conduction mechanism of charge carriers. The gradual increase in activation energy with increasing Zr concentration suggests modifications in the oxygen ion transport pathway and charge carrier mobility within the perovskite lattice. The comparatively low activation energy values indicate favorable oxide ion conduction and enhanced electrochemical behavior. Among all samples, Zr₄ exhibits the highest conductivity and improved charge transport properties due to the enhanced formation of oxygen vacancies. These results confirm that Zr substitution improves the electrical conductivity and electrochemical performance of BSCF cathodes suitable for intermediate-temperature solid oxide fuel cell (IT-SOFC) applications.

The ASR values decreased with increasing temperature due to enhanced oxygen reduction kinetics. [4] Lower ASR values indicated improved electrochemical activity of the cathode materials. [16] Ti and Zr substitution reduced ASR by increasing oxygen vacancy concentration and ionic conductivity. [19] The decrease in ASR at elevated temperatures confirmed thermally activated electrode processes. [18] The porous cathode microstructure significantly contributed to reduced ASR values. [23] Enhanced oxygen ion diffusion and charge transfer kinetics resulted in lower ASR values. [7] The reduction in ASR confirmed improved cathode–electrolyte interfacial properties. [17] The impedance spectra showed smaller semicircle diameters for doped samples, indicating lower ASR. [12] The ASR behaviour strongly depended on oxygen vacancy concentration and electrode microstructure. [21] The lowest ASR values were observed for

optimally doped BSCF cathodes, indicating superior electrochemical performance.[12]

Conclusions:

The synthesized Ti and Zr doped BSCF cathode materials exhibited excellent structural, thermal, morphological, and electrochemical properties suitable for intermediate temperature Solid Oxide Fuel Cell (ITSOFC) applications.

1. XRD Results

All Ti and Zr doped BSCF samples exhibited a single phase cubic perovskite structure. No secondary impurity phases were detected, confirming successful dopant incorporation. Crystallite sizes remained in the nanocrystalline range (~38–42 nm). Ti and Zr substitutions maintained structural stability with only slight lattice parameter variations.

2. SEM Results

SEM images revealed porous and interconnected grain morphology favorable for oxygen diffusion. Uniform grain distribution and Nano sized particles were observed. The microstructure supports enhanced electrochemical activity and oxygen ion transport.

3. SEM–EDAX Results

EDAX confirmed homogeneous distribution of Ba, Sr, Co, Fe, Ti/Zr, and O elements. The obtained elemental composition closely matched the nominal stoichiometric ratios. No impurity peaks were observed, indicating good phase purity.

4. TGA Analysis

All samples showed low total weight loss (<2%), confirming excellent thermal stability. Weight loss at higher temperatures was associated with oxygen vacancy formation and lattice stabilization. Zr doped samples exhibited comparatively better thermal stability.

5. DTA Analysis

Thermal transitions near 540°C –560°C corresponded to crystallization and perovskite phase formation. Both Ti and Zr doped samples exhibited stable thermal behavior and controlled oxygen release. The results confirmed suitability for intermediate temperature SOFC operation.

6. Electrical and Impedance Analysis

Grain resistance (R_g) decreased with increasing Ti and Zr concentration. Improved ionic and electronic conductivity was observed due to enhanced oxygen vacancy concentration. The electrochemical performance of doped BSCF cathodes improved significantly with substitution.

Overall Conclusion

Ti and Zr doped BSCF cathodes synthesized by the sol–gel method demonstrated excellent phase stability, thermal stability, nanoscale morphology, and enhanced electrochemical conductivity. The obtained results confirm that the synthesized cathode materials are highly suitable for Intermediate Temperature Solid Oxide Fuel Cell (ITSOFC) applications.

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