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Studies on $Gd_{1-x}Ba_xCoO_3$ Cathode Material for Solid Oxide Fuel Cells

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ABSTRACT: The $Gd_{1-x}Ba_xCoO_3$ systems were synthesized by assisted combustion method which using Gadolinium (III) nitrate, Barium (II) nitrate, Cobalt(III) nitrate and aspartic acid. The above mixture solution was heated at $80^\circ C$ until gel formation and it became foamy powder. Further it was claimed at $600^\circ C$ for 6 hrs. Finally we get $Gd_{1-x}Ba_xCoO_3$ Nano crystalline powder. The structure of $Gd_{1-x}Ba_xCoO_3$ was confirmed by XRD Studies. The surface morphology was confirmed by SEM. The thermal analysis of the synthesized product was obtained by TGA and DTA. The conductivity was determined by four probe method.

KEYWORDS: Assisted Combustion, XRD, SEM, Conductivity.

I. INTRODUCTION

The focus of research in Solid Oxide Fuel Cell Technology as new power generation device due to their high conversion efficiency, low emissions and excellent fuel flexibility. The intermediate operating temperature range from $500^\circ - 700^\circ C$, it leads to a significant decrease in electrode activity. The considerable reduction in reaction temperature and time in this recent synthesis. It has interesting effect in the particle growth during reaction and the resulting particle size of the product is usually reduced efficiently.

The porous SOFC cathode is used for the adsorption of oxygen molecules, their dissociation into oxygen atoms, oxidation by charge exchange and entry of the resultant ion into the dense electrolyte layer. Thus, a cathode material should possess: (a) broad electrochemical reaction zone, (b) possibility for created oxygen ions to be transported away from the reaction site into the bulk of the electrolyte, (c) good electronic conductivity, (d) stability under application conditions and (e) a thermal expansion coefficient compatible with that of the solid electrolyte.

A Potential Cathode material must exhibit electronic as well oxygen ion conductivity to increase the triple phase boundary which enhances the efficiency of SOFCs. In addition, the material should exhibit catalytic activity and compatible mechanical properties. In this method, reduction-diffusion was used to synthesize exchange coupled $Gd_{1-x}Ba_xCoO_3$ Nanocomposites in < 100 nm size range.

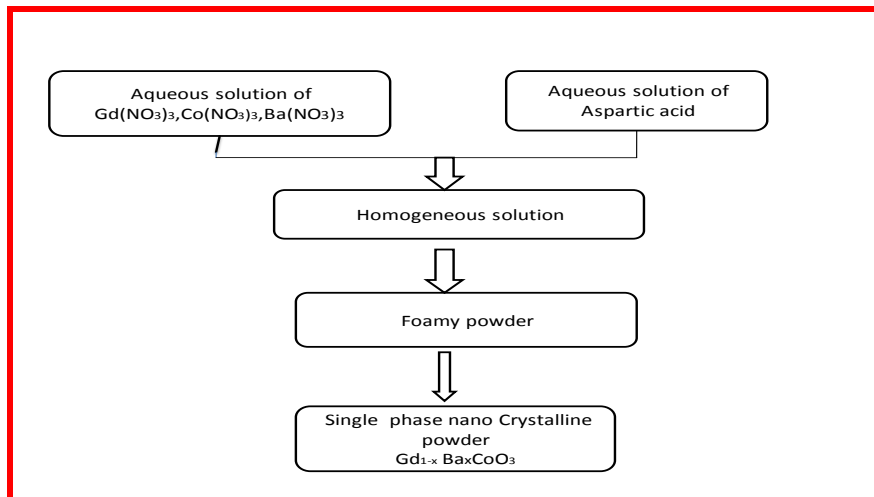
A wide variety of processes are available for the synthesis of ceramic powders. Among the various synthetic approaches, solid state synthesis requires a high calcin and grinds the powder mixture in order to achieve the desired homogeneity. Therefore, the risk of contamination from the grinding media is greater in this process. In general, we chemical processes are capable of producing high purity, homogeneous and ultrafine powders at lower temperature. The synthesis of ceria powder by various wet chemical routes, such as the co-precipitation, hydrothermal solution and the combustion routes has been reported. In the combustion route a self-sustaining exothermic redox reaction between a fuel (such as aspartic acid) and an oxidant (nitrate salts of metals) is allowed to take place. The fuel also acts as a complexing agent in the aqueous solution of nitrate salts. On heating the solution, a gel is formed as an intermediate before the combustion reaction starts. Hence, the process is also known as gel combustion.

The present work Ba-doped GdCoO_3 was aimed to improve the electrochemical properties for ITSOFCs cathode applications, it has prepared by assisted combustion technique. The prepared samples were characterized by XRD, SEM, TGA, and DTA. We report on the results of a complete characterization study including the electrical performance of the single cells, conductivity and the structural characterization from data, which is powerful to that the electrode materials under the usual conditions of a SOFC. In complement, Thermogravimetry analysis (TGA) was used to demonstrate the reversibility of the $\text{Gd}_{1-x}\text{Ba}_x\text{CoO}_3$ oxidized and reduced phases.

II. EXPERIMENTAL

Assisted combustion synthesis of Nanocrystalline $\text{Gd}_{1-x}\text{Ba}_x\text{CoO}_3$ ($x=0, 0.1, 0.3, 0.5$) powder

We used Gadolinium nitrated $(\text{NO}_3)_3$ (99.9%), Barium nitrate $\text{Ba}(\text{NO}_3)_2$ (99.99%) and Cobalt Nitrate $\text{Co}(\text{NO}_3)_2$ (99.9%) were purchased from Sigma-Aldrich. All of the Chemicals were used without further purification



III. CHARACTERIZATION

The initial characterization of the product was carried out by XRD with JEOL JSM-840 which the geometry of $\text{Cu K}\alpha$ radiation ($\lambda = 1.5404 \text{ \AA}$). All prepared Samples were subjected to structural characterization by X-ray powder diffraction (XRD). A curved graphite crystal was used as a monochromator. The X-ray diffraction measurements were carried out in a 2θ range from 10° to 80° respectively. Thermal analysis was carried out in a Mettler TA3000 system equipped with a TC10 processor unit. Thermo gravimetric curves were obtained in a TG50 unit, which working at a heating rate of $10^\circ \text{ C min}^{-1}$. The experimental measurements were carried heating from 25° to 500° C with a rate of $20^\circ \text{ C min}^{-1}$ for powder samples.

Electrical conductivity measurements, we use of the sintered samples are required. Disk-shaped pellets were used. The pellet were initially heated in air. The electrical conductivity of the $\text{Gd}_{1-x}\text{Ba}_x\text{CoO}_3$ Cathodes is presented. All the samples show a decrease in electrical conductivity with increasing temperature, showing the metallic behaviour over the entire temperature range. Their conductivities start to decrease significantly at about 300° C , due to such lattice defects breaking the Co-O-Co bonds resulting in a loss of oxygen atoms from the lattice and reduction of Ba^{4+} to Ba^{3+} .

IV. RESULTS AND DISCUSSION

Typical X-ray powder diffraction (XRD) patterns of $\text{Gd}_{1-x}\text{Ba}_x\text{CoO}_3$ with $x=0, 0.1, 0.3, 0.5$ are shown in XRD Spectrum respectively.

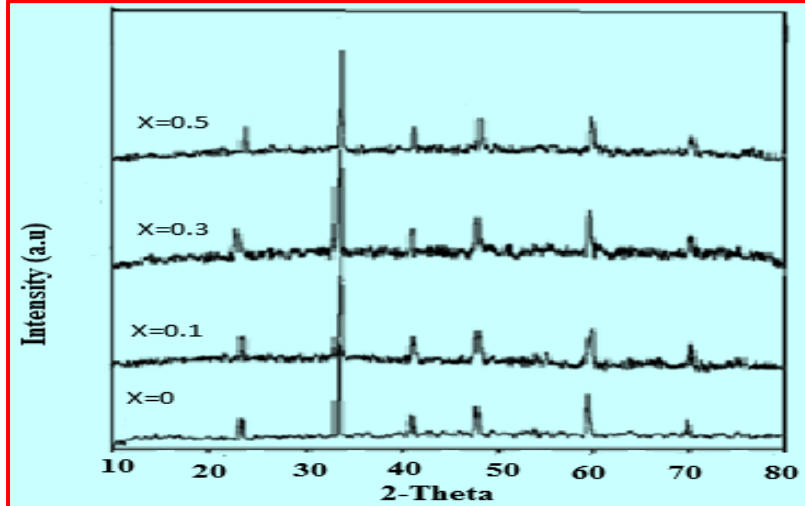
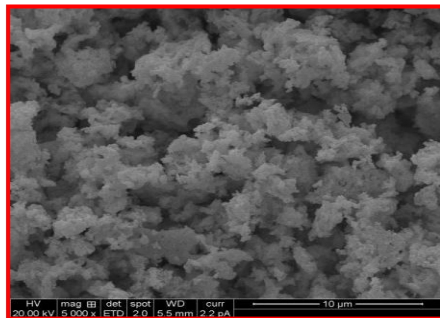


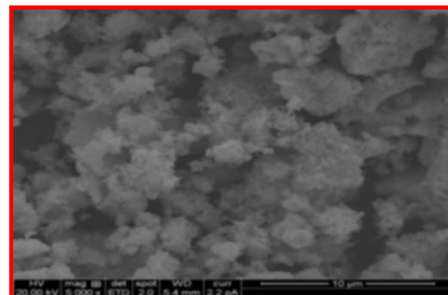
Fig-1.XRD pattern of $Gd_{1-x}Ba_xCoO_3$

In general all the diffracted lines were broader than the usual ones it observed for highly crystalline solids. The oxidized and reduced $Gd_{1-x}Ba_xCoO_3$ perovskites were obtained as well as crystallized powders. Orthorhombic structures were identified from X-ray diffraction for the oxidized and reduced materials respectively. The broadening in the diffracted peaks was attributed to the super fine crystalline nature of composites. The XRD patterns as prepared $Gd_{1-x}Ba_xCoO_3$ powders revealed that the formation of well Nano-crystalline single phase materials. Detect the crystallite size of all compositions under study, determined using the values are high score plus software based on the following expression.

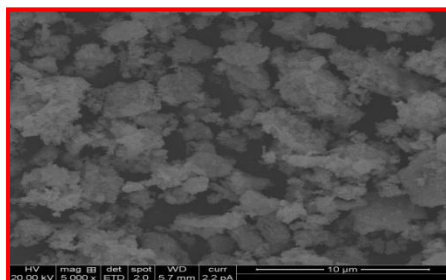
$$D = 0.9\lambda / \beta \cos\theta$$



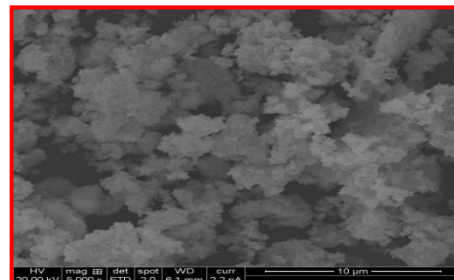
(a)



(b)



(c)



(d)

Fig2.(a) SEM Photograph of as-prepared $GdCoO_3$ (b) SEM Photograph of as-prepared $Gd_{0.9}Ba_{0.1}CoO_3$
(c) SEM Photograph of as-prepared $Gd_{0.7}Ba_{0.3}Co$ (d) SEM Photograph of as-prepared $Gd_{0.5}Ba_{0.5}CoO_3$

The SEM Photograph of the cleaved surface of composite cathode and magnified view of cathode it displayed in the Spectrum respectively. It can be seen that powder contained nanoparticles with the size of the particle is < 30 nm. This is evidence for the Compatibility of GdCoO₃ Cathode material. The displayed at the figure is x= 0, 0.1, 0.3, 0.5 respectively. A close looks at the figures also reveals that the grain size increase with increase in x.

The electrical conductivity of the Gd_{1-x}Ba_xCoO₃ Cathodes is presented in the temperature range is 100-750°C dc four probe method. The entire sample has shown a decrease in electrical conductivity with increasing temperature for metallic behavior over the entire temperature range. Their conductivities start to decrease significantly at about 300°C due to such lattice defects breaking Ba-O-Ba bonds, resulting in loss of oxygen atoms from the lattice and reduction of Co⁴⁺ to Co³⁺.

The thermal evolution of the samples was studied under both reducing and oxidizing atmosphere. The TGA and DTA Spectrum obtained on GdCoO₃ Cathode Powder. The major weight loss occurs in between 100-300°C. In the TGA pattern the GdCoO₃ Sample showed a weight loss of about 0.035mg/min until 81.32°C. The Sample on further heating from 81.32°C-280.94°C Showed slight weight gain and weight loss of about 0.035mg/min in 280.94°C. Again the Sample showed a weight increase from 310°C-480°C and then a weight loss of 0.041mg/min during further heating up to 480.50°C. The weight gain and weight loss indicated that the GdCoO₃ powder exhibited easy reversible absorption-desorption of oxygen from air.

The DTA analysis was performed in air from 40-730°C at 20°C min⁻¹, the thermal analysis suggested. The existence of a Co²⁺/Co³⁺ mixed Valence in the reduced phase, for the determined oxygen contents an average valence of 1.28+ was obtained for Co.

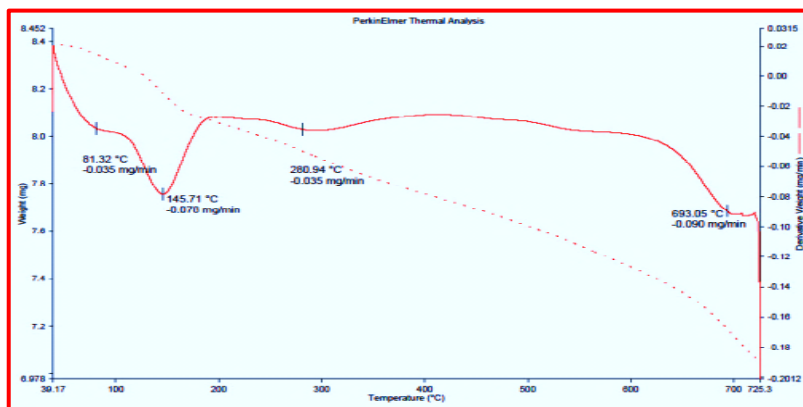


Fig3.TGA and DTA Spectra of GdBaCoO₃

Electrical conductivity measurements, we use of the sintered samples are required. Disk-Shaped pellets were used. The pellets were initially heated in air. The electrical conductivity of the Gd_{1-x}Ba_xCoO₃ Cathodes is presented. All the samples showed a decrease in electrical conductivity with increasing temperature, showing the metallic behavior over the entire temperature range. Their conductivities start to decrease significantly at about 250°C, due to such lattice defects breaking the Co-O-Co bonds resulting in a loss of oxygen atoms from the lattice and reduction of Ba⁴⁺ to Ba³⁺.

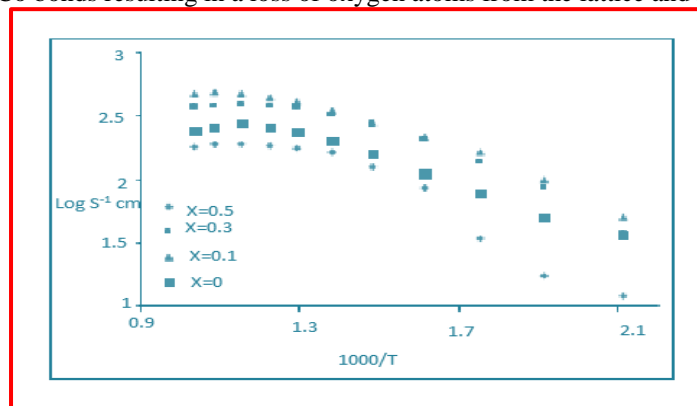


Fig4. Conductivity of GdBaCoO₃



All the samples show a decrease in electrical conductivity with increasing temperature, showing the metallic behavior over the entire temperature range. Their conductivities start to decrease significantly at about 300^oc, due to such lattice defects breaking the Co-O-Co bonds resulting in a loss of oxygen atoms from the lattice and reduction of Ba⁴⁺ to Ba³⁺.

V. CONCLUSION

A combustion synthesis process has been used to prepare Gd_{1-x}Ba_xCoO₃ Nano crystalline powder. According to our results thermal behavior, phase formation and crystallite size are strongly dependent on the nature of the fuel (aspartic acid) and heating temperature. The combustion reaction is more complete with aspartic acid, attaining moderate temperature and generating less organic residues. Gd_{1-x}Ba_xCoO₃ phase formation, with secondary phases, was observed when aspartic acid was used as fuel because the reaction is less violent, promoting increased formation of gases which greatly contributes to obtain materials of high crystallinity with nonmetric dimensions. The synthesized nano powders have nano particles with high specific area. In addition electrical conductivity measurement revealed that the maximum conductivity of 450 Scm⁻¹ was obtained in air at 600^oC which is higher than the reported values.

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