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Facile Synthesis of Ceria Based Ceramic Nanorods by Citrate gel route

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Abstract

Nano structured CeO_2 has attracted much attention due to its redox properties, transport properties and high surface to volume ratio with respect to bulk materials. Trivalent ion doped ceria systems have better properties than the pure ceria systems. The present paper discusses the structural properties of nanostructured gadolinium doped ceria (GDC) co doped with Bi synthesized by citrate gel method. Phase pure samples are obtained, which is shown in the X-ray diffraction patterns. Presence of Ce, Gd and Bi in the samples is identified using Fourier transform infrared spectroscopy and energy dispersive spectroscopy. Scanning electron microscopic images show that nanorod shaped grains are obtained for the system. Nanorod shaped structures can yield better ionic conductivity.

Key words : Nanocrystalline materials, ceria, nanorods, citrate gel synthesis, solid electrolytes, solid oxide fuel cells.

1. Introduction

Nano structured cerium oxide (CeO_2) based materials are highly useful for solving energy related environmental issues[1]. CeO_2, the most abundant rare earth oxide[2], is a technologically important material due to its wide applications as oxygen sensors[3], for elimination of toxic auto exhaust gases[4], electrolyte and catalyst in solid oxide fuel cells (SOFC)[5,6], glass polishing materials as well as elements for environmental chemistry and medicine [7]. The production of clean energy by environment friendly ways is one of the potential areas of research. SOFCs are eminent candidates for energy production through environmentally clean electrochemical reaction between a fuel and an oxidant.

Ceria based fast ion conductors are primarily used as solid electrolytes in intermediate temperature SOFCs (ITSOFC)[8,9]. These electrolytes require high sintering temperature (>1300^{o}C) for achieving densities up

to 90% or more compared to theoretical value, in order to exclude open porosity and reactant crossover[5,10]. But, high sintering temperature leads to the reduction of CeO_2 to Ce_2O_3 ($Ce^{4+} \rightarrow Ce^{3+}$), which results in loss of efficiency and depletion of open circuit voltage of the cell. The development of simple and cost effective synthesis and fabrication process for ceria based nanomaterials are essential for SOFC applications. The sintering temperature of ceria based electrolytes can be reduced by synthesising nanostructured materials using sintering aids[11]. Bi(trivalent) is identified as a good sintering aid for the production of ceria solid electrolytes. The present work, discusses the synthesis of $Ce_{0.8}Gd_{0.1}Bi_{0.1}O_{2-\delta}$ nanoparticles by low cost citrate gel method. The structural properties of the synthesized materials are investigated using X-ray diffraction (XRD) technique, Williamson and Hall plot analysis, Fourier transform infrared (FT-IR) spectroscopy, Energy dispersive spectroscopy (EDS) and Scanning electron microscopy (SEM).

2. Methodology :

The chemicals used for the preparation of $Ce_{0.8}Gd_{0.1}Bi_{0.1}O_{2-\delta}$ are Cerium nitrate ($Ce(NO_3)_3.6H_2O$), Gadolinium nitrate ($Gd(NO_3)_3$) and Bismuth nitrate($Bi(NO_3)_3$) (all are analytical grade with purity 99.9%). In citrate gel method, stoichiometric amount of each nitrate was dissolved in distilled water and mixed with equimolar amount of citric acid. All the reactants were mixed well in a beaker by stirring for 10 minutes and placed in a hot air oven for evaporation. The obtained foam like material was crushed and calcined at 600^{o}C for 3 h.

The calcined samples were ground well and pelletized using hydraulic press by applying 2.5 MPa pressure. The pellets (~ 9mm diameter with different thickness) were sintered at 900^{o}C. The sintering time for pellets was 5 h. The pellets have a relative density determined using Archimedes' Principle is of about 85% after sintering.

X-ray diffraction for the sintered powder samples was carried out using X-rays of 1.54060 Å wavelength in the angular range 10^o-90^o and average crystallite size of the two samples was determined by the Scherer's equation[14-16]. The mean size and strain within a powder can be calculated from the diffraction pattern using the Williamson and Hall plot (H-W plot)[17] even when both are present simultaneously. Infrared spectroscopy (FT-IR) makes use of vibrational energy levels of atoms in the molecule and based on which, it identified the components in the mixture and the quality or consistency of the sample. The stoichiometry and chemical combination of the sintered samples were examined using energy dispersive spectroscopy. Scanning electron microscopy utilizes a convergent electron beam to scan the surface of the sample and gave information about the morphology, grain size and the amount and nature of grain growth in the sintered samples.

3. Result and Discussion

X-ray diffraction analysis :

The X-ray diffraction patterns of $Ce_{0.8}Gd_{0.1}Bi_{0.1}O_{2-\delta}$ (Bi-GDC) samples synthesized by citrate gel methods are shown in Figure.1. The substitution of Ce^{4+} with Gd^{3+} and Bi^{3+}, with difference in valance and ionic radii, expects the production of more oxygen ion vacancies in the crystal lattice with increased lattice parameter. For comparison, XRD patterns of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (GDC) is also shown in Figure 1. The patterns have cubic fluorite structure of CeO_2 [JCPDS file no: 75-0162] with slightly different lattice parameters. This infers that the dopants are completely merged into the crystal structure of ceria producing more oxide ion vacancies as expected. The diffraction peaks are broad; showing nano-dimensions of the samples on crystallization[10,13,15]. The lattice parameter and crystallite size are enumerated in Table 1. The currently synthesized samples have positive deviation in lattice constant compared to the reported values for gadolinium (20%) doped ceria. The ionic conductivity of the samples may be greater at intermediate temperature region, since there is the production

of more anionic vacancies and increased lattice size.[5,11,18].

Table1. Comparision of parameters using XRD analysis and H-W analysis

Sample	XRD analysis		H-W analysis	
	Crystallite Size, D(nm)	Lattice Parameter, a(Å)	Crystallite Size, D(nm)	Lattice strain, ε
$Ce_{0.8}Gd_{0.1}Bi_{0.1}O_{2-\delta}$	16.67	5.46±0.02	12.23	0.0017
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	14.50	5.47±0.06	12.47	0.00159

Williamson –Hall Plot Analysis :

Figure 2 shows the H-W plots of pure and Bi co-doped Gadolinium doped Ceria samples. H-W plots are used, since the sample is nano-crystalline and has isotropic nature[17]. It relies on the principle that the approximate formulae for size broadening, β_D, and strain broadening, β_ε , vary quite differently with respect to Bragg angle, θ in such a way that,

$$\beta_D = 0.9\lambda/D \cos\theta \quad (1)$$

$$\beta_\varepsilon = 4\varepsilon \tan\theta \quad (2)$$

where D is the crystallite size and ε is the strain of the powder sample and λ is the wavelength of X-ray used for diffraction[17].

The convolution of equations (1) and (2) is assumed by Williamson and Hall to give an equation of straight line,

$$\beta\cos\theta = 4\varepsilon \sin\theta + 0.9\lambda/D \quad (3).$$

By plotting βcosθ against 4sinθ, the intercept with Y-axis gives the crystallite size and slope of the fitted line gives the lattice strain directly. The parameters determined from H-W plot are given in Table.1. The crystallite size determined from the plot matches with the value calculated from XRD pattern. Lattice strain can be considered as the measure of effect of distortions (doping) made to the lattice. In our sample, strain arises also due to the increased number of grain boundaries in the nanocrystalline sample.

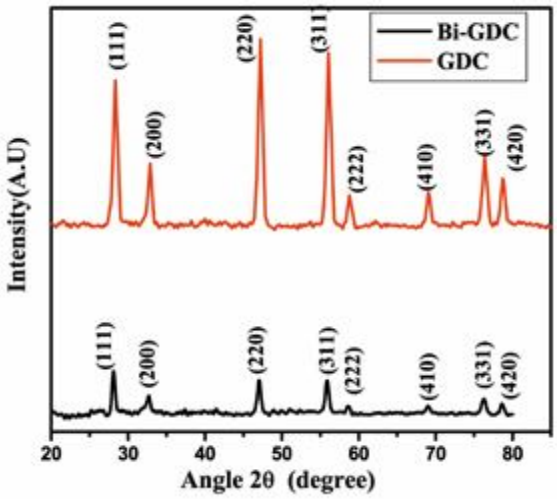

Figure.1.: XRD patterns of $Ce_{0.8}Gd_{0.1}Bi_{0.1}O_{2-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ prepared by citrate gel method

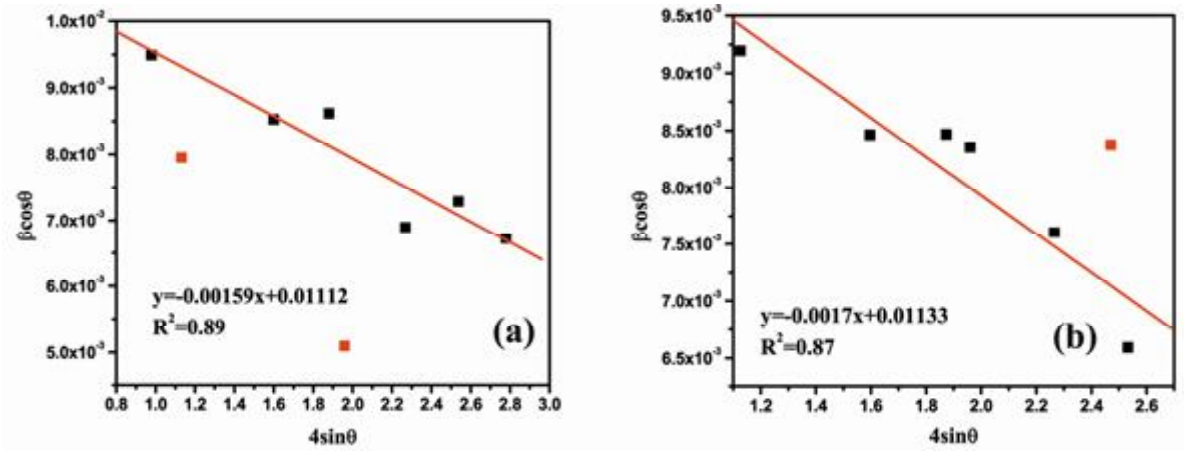

Figure.2.: H-W plots of (a) $Ce_{0.8}Gd_{0.1}Bi_{0.1}O_{2-\delta}$ and (b) $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ prepared by citrate gel method

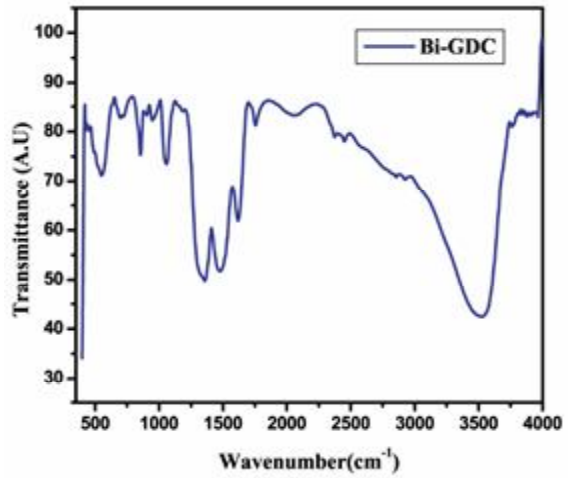

Figure.3.:FT-IR spectrum of $Ce_{0.8}Gd_{0.1}Bi_{0.1}O_{2-\delta}$ prepared by citrate gel method

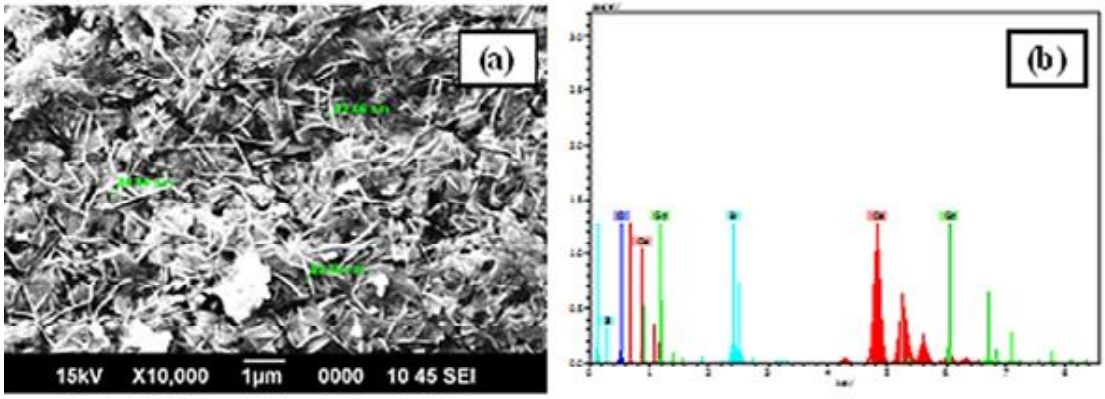

Figure.4.:(a)SEM image and (b) EDAX spectrum of $Ce_{0.8}Gd_{0.1}Bi_{0.1}O_{2-\delta}$ prepared by citrate gel method

FT-IR spectroscopic analysis :

The FTIR spectrum of the samples is shown in Figure.3. The strong band near 840 cm^{-1} shows the presence of Bi-O bond stretching vibrations. The band below 450 cm^{-1} and 550 cm^{-1} show the presence of cerium and gadolinium respectively in the synthesized samples. The broad band near 3000 cm^{-1} is mainly due to the O-H stretching vibration and band near 1650 cm^{-1} and 1300 cm^{-1} is mainly due to O-C-O stretching frequencies.

Scanning electron microscopic analysis :

The surface morphology of the samples is studied using SEM images shown in Figure.4. The pellets shrunk and attained moderate density after sintering at 900^{o}C. From the image, it is clear that all the sintered pellets have rod-shaped grains with different dimensions. The size and shape of grains can be considered as functions of sintering temperature and sintering time. The grain-size is 82-89 nm for the samples respectively. The size and shape of grains as well as the homogeneity in grain size have strong effects on the electrical conductivity of nanostructured materials[19]. The rod shaped grains are expected to have more conductivity than the round shaped grains

The chemical constituents and their stoichiometry of the samples are identified using Energy dispersive spectroscopy **(**EDS). The sample contains cerium, gadolinium, bismuth and oxygen in expected stoichiometry as shown in Figure.4.

4. Conclusion

The pure single phase nanocrystalline $Ce_{0.8}Gd_{0.1}Bi_{0.1}O_{2-\delta}$ is successfully synthesized by cost effective citrate gel synthesis method. The line broadening of peaks and absence of secondary phases in the XRD pattern confirms the formation of cubic fluorite structured nanocrystalline powders. Reduction in the sintering temperature is achieved due to the addition of trivalent ion Bi^{3+}, having similar ionic radius as that of Ce^{4+} and Gd^{3+}. Due to the large surface to volume ratio in nano-phase, the synthesized sample may have greater ionic conductivity. The economic citrate gel route produced rod-shaped grains on low temperature sintering at 900^{o}C. The synthesis method has greater influence on the size and shape of grains. Hence, the synthesis method discussed can be used for the economic production of doped ceria, useful as fast ion conductors and catalyzers. Further studies on the ionic conductivity and catalytic activity of the synthesized sample are required for confirmation.

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