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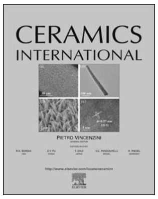

Influence of rare earth (RE=Nd, Y, Pr and Er) doping on the microstructural and optical properties of ceria nanostructures

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ABSTRACT

Nanopowders of $Ce_{0.9}RE_{0.1}O_{1.95}$ (RE=Nd, Y, Pr and Er) were synthesized by nitrate-fuel combustion method and calcinated at 700 °C for 2 h to obtain completely crystalline structures. The effect of RE dopants on the crystalline nature, lattice parameters, and microstructural parameters such as microstrain, stress, and deformation energy density of ceria was evaluated through uniform deformation model (UDM), uniform deformation stress model (UDSM) and uniform deformation energy density model (UDEDM) by using the X-ray diffraction (XRD) data. The results revealed that the microstructural parameters were considerably altered with respect to the dopants. The transmission electron microscope (TEM) graphs and their corresponding selected area diffraction (SAED) patterns of ceria nanoparticles confirmed that all doped ceria powders are crystalline with the wide range of particle size distributions aligned in all the directions. The optical diffuse reflectance spectroscopy (DRS) measurements showed a band at around 340 nm attributed to the transitions of charge-transfer between O 2*p* and Ce 4*f* orbitals in cerium oxide and RE doped CeO_2 exhibited the reflectance band in the visible regions due to the transition of 4*f* energy levels of RE ions. Photoluminescence (PL) spectra of RE doped ceria showed the blue-green emission bands.

1. Introduction

The expected properties of solid oxide fuel cell (SOFC) such as high energy conversion efficiency, multi-fuel capability, operating at low temperature, simplicity of system design [1] have made the ceramics based on cerium oxide (CeO_2) of great interest. Conductivity of nanocrystalline materials is increased with decreasing grain size, so nanopowders are preferred to fabricate SOFC´s components. Insertion of trivalent rare earth (RE) ions into ceria lattice is a simplest way to modify its electronic structures which resulted in having excellent oxygen storage behavior [2,3], and improved the optical emission characteristics of host matrix [4]. In addition, doping of RE ions in ceria lattice leads many industrial technological applications such as catalysis [5], high temperature resistance coatings [6], UV blockers [7] luminescent materials [8] and solid oxide fuel cells [9]. Specifically, the insertion of Nd, Y, Pr and Er ions into ceria lattices is expected to improve their physical and chemical properties for various industrial applications. For instance, band gap alteration, visible and near infrared emission have been enhanced upon the doping of various RE ions into the ceria lattice [10,11]. Similarly, considerable improvement on the efficiency of photocatalytic activities against various organic pollutants with respect to different metal ions has been achieved [12,13]. There are different solid solution syntheses methods are available to prepare doped ceria nanopowders. The nitrate-fuel combustion synthesis is a simple and time saving technique for preparing various ceria solid solutions doped with different metallic oxides [14–18]. To achieve and control the desirable properties of the nanomaterials, it is necessary to evaluate their microstructure, electronic structure, morphology, porosity and particle size distribution.

X-ray diffraction (XRD) peak profile analysis is often used to characterize the microstructure of crystalline materials, in particular to determine the mean crystallite size, dopant induced lattice strain and stress [18]. In polycrystalline structural powders, the deviation from the perfect crystallinity leads to a broadening of the diffraction peaks [19]. X-ray diffraction peaks are broadened by decreasing grain-size and increasing lattice distortions caused by lattice defects, which can be measured via Williamson-Hall (W-H) method to estimate both size-induced and strain-induced broadening [20].

Owing the importance of RE doped ceria in various industrial applications, herein, we have synthesized RE ions doped ceria via nitrate-fuel combustion route. The influence of RE ions on the microstructural parameters such as lattice strain, stress and deforma-

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tion energy density has been studied. Furthermore, we have explored the effect of RE ions on the optical properties of ceria.

2. Experimental

Nitrate-fuel combustion method was applied to prepare different rare earth doped ceria as $Ce_{0.9}Nd_{0.1}O_{1.95}$(NDC), $Ce_{0.9}Y_{0.1}O_{1.95}$(YDC), $Ce_{0.9}Pr_{0.1}O_{1.95}$(PDC) and $Ce_{0.9}Er_{0.1}O_{1.95}$ (EDC), where Ce, Nd, Y, Pr and Er are Cerium, Neodymium, yttrium, praseodymium and Erbium, respectively. Citric acid was used as an organic fuel and high purity metallic nitrates (> 99.9%) of Ce, Nd, Y, Pr and Er were used as precursor reagents. The synthesis condition was maintained equally and the same molar percent of each rare earth metallic oxide, 10 mol%, was considered to produce all nanopowders. The details of the method have been reported elsewhere [15,17,18,21,22]. The as-synthesized powders were calcined at 700 °C for 2 h to obtain completely crystalline structures and then targeted for to study systematically.

The crystalline structure of NDC, YDC, PDC and EDC was analyzed by X-ray diffraction technique using a Siemens D5000 diffractometer with CuK_α radiation, operating at 40 kV and 20 mA. The 2θ step size was 0.02° with the integration time of 1 s. Microstructural observations, selected area electron diffraction (SAED) patterns and nanoparticle size distribution measurement were carried out by transmission electron microscopy (TEM, JEOL JEM 2000 EX). All the samples were prepared by dispersing the powder in dilute ethanol medium under ultrasonic agitation. A drop of suspension was placed on a carbon coated fine mesh copper grid that after evaporation of ethanol was used as test sample. The incorporation of dopant and emission characteristics of the prepared nanostructures were analyzed through diffuse reflectance (DRS) and photoluminescence (PL) spectroscopies at room temperature. The absorption spectra were recorded by using UV–visible spectrophotometer (UV-2600 Shimadzu-Japan)*,* in the range of 200–900 nm and the steady state PL measurements were done using a *Perkin Elmer* fluorometer with xenon lamp at an excitation wavelength of 340 nm.

3. Result and discussion

3.1. Phase analysis

The X-ray diffraction patterns of the calcined pure and RE doped ceria powders presented in Fig. 1(a), All the diffraction peaks are indexed well with the fluorite crystal structure [23,24] and the spectra did not show any impurities peaks related to the dopant RE^{3+} oxides within the detection limit of XRD, which indicating the formation of single phase fluorite crystal structure of ceria. The peaks are located at the angles (2θ) of 28.59, 33.10, 47.53, 56.35, 59.22, 69.41, 76.67 and 79.23° which corresponded to the (111), (200), (311), (222), (400), (331) and (420) planes, respectively, of ceria (JCPDS no: 65-5923). The diffraction peaks of Nd doped ceria nanostructures showed a lower angle shift. Usually, ionic radius of doping ion is bigger than the host ion causes lattice expansion, whereas ionic radius of doping ion is smaller than the host ion causes lattice compression. In the present case, ionic radius of RE dopant of Nd^{3+}(1.109 Å) are bigger than the host Ce^{4+}(0.970 Å), which leads to lower angle and lattice expansion.

In general, the concentration of foreign atoms, external strain and the difference of the ionic radii with respect to the substituted matrix ion, and defects presents in the system are significantly alter the lattice parameters of the materials [25]. The lattice parameters '*a*' axis and unit cell volume '*v*' are calculated by using the formulae [26],

$$a = d\sqrt{h^2 + k^2 + l^2} \text{ and } v = a^3 \tag{1}$$

The effect of RE^{3+} ions on the lattice parameters of '*a*' axis and the unit cell volume '*v*' is shown in Fig. 1(b).

3.2. Microstructural calculation

X-ray line profile analysis is a simple and powerful tool to identify the presence of dopant ion in the host lattice and quantify the microstructural parameters like crystallite size and lattice strain. Williamson-Hall had proposed the diffraction peak broadening is the sum of crystallite size and strain as a function of diffraction angle and it can be deduce in the mathematical expression [27],

$$\beta_{hkl} = \beta_t + \beta_\varepsilon \tag{2}$$

where, β_t is due to crystallite size, β_ε is due to strain present in the system and β_{hkl} is the width of the half maximum intensity of diffracted peak. Usually, the broadening of each diffracted line is a combination of instrumental and sample. The standard silicon (*Si*) sample was used to eliminate the effects of line broadening from the instrumental contribution. The instrumental corrected line broadening of each diffraction peak is deduced through the following relation [28],

$$\beta_{hkl} = [(\beta_{hkl})^2{}_{measured} - (\beta_{hkl})^2{}_{instrumental}]^{0.5} \tag{3}$$

where, $\beta_{instrumental}$ is the instrumental broadening and $\beta_{measured}$ is the broadening from the sample. To quantify the full width at half maximum (FWHM) of each diffraction line, the peaks were fitted using Lorentzian function. The crystallite size (t) contribution can be calculated by using Scherer formula [29],

$$\beta_t = \frac{k\lambda}{t\cos\theta} \tag{4}$$

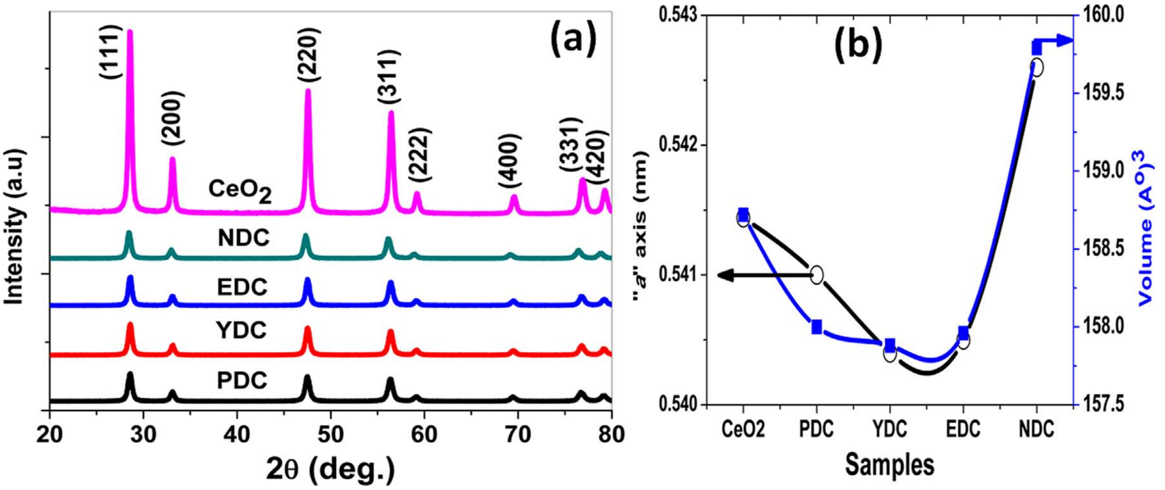

Fig. 1. (a) XRD diffraction patterns of pure and RE doped ceria nanostructures **(b)** Variation of lattice parameter on '*a*' axis and unit cell volume (*v*).