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Effect of rare earth dopants on structural characteristics of nanoceria synthesized by combustion method

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ABSTRACT

Rare earth (RE)-doped ceria powders with a chemical composition of $Ce_{1-x}RE_xO_{2-x/2}$ (X: 0.1 and RE: Gd, Sm, Er, Pr, Nd and Y) were prepared by nitrate-fuel combustion method. The TG and DT analyses of the as-synthesized powders showed a complete combustion with a small range endothermic process within a broad exothermic reaction. GDC, SDC, EDC, PDC, NDC and YDC precursors were calcined at 700 °C for 2 h and characterized using XRD, SEM and TEM. Powder characteristics such as morphology, crystallite size, primary particle size, lattice parameter and lattice strain of calcined powders have been studied. All X-ray diffraction patterns of as-synthesized and calcined samples were indexed as fluorite structure. The crystallite size of nanoceria obtained by Scherrer's formula was between 17 and 19.5 nm and via Williamson–Hall (W–H) plots in the range of 25–38 nm that shows the effect of lattice strain on the average crystallite size. Primary particle size calculated from BET data was in the range of 24–37 nm. TEM images showed fine spherical particles and SAED patterns confirmed fluorite structure of all powders.

1. Introduction

Ceria (CeO_2) is a highly refractive ceramic material possessing the cubic fluorite crystal structure in its pure form or doped with ions [1,2]. Doping ceria with suitable trivalent cations results in having excellent oxygen storage behavior [3]. This behavior results from the balance between reduced and oxidized states of ions i.e., Ce^{3+} and Ce^{4+} and from increased oxygen transport capacity [4,5]. Chemical–mechanical polishing for microelectronics, UV filter [6], electrolytes for solid oxide fuel cells (SOFCs) [7–9], oxygen pumps, ampere metric oxygen monitors [10,11], luminous materials [11], sunscreen cosmetics [12], three way catalysts for the treatment of automotive exhaust gases, petroleum cracking catalyst and gas sensor [13,14] are some application of these ceria based ceramics.

Selecting rare earth (RE) elements such as Nd, Sm and Gd [15] as dopants for ceria and substitution of Ce^{4+} in ceria by these trivalent cations distorts the lattice structure and generates oxygen vacancies. As a consequence, chemical stability and ionic conductivity are increased and the reducibility is suppressed [3,5,16]. In addition, doping RE-oxide into CeO_2 can slightly improve mechanical properties [17]. RE-doped ceria with higher oxygen ion conductivity than that of yttria-stabilized zirconia (YSZ) [18] has attracted much attention to be the most promising material for serving as a solid electrolyte material for intermediate and low temperature SOFCs [19,20].

Different techniques such as hydrothermal [21], co-precipitation [22], sol–gel [23], spray-pyrolysis [24] and combustion [15,25–27] have been used and reported to synthesis doped ceria nanopowders. Compared with many chemical routes, combustion synthesis is a simple, feasible and less time consuming technique for preparing various oxide ceramics with the ability of direct and precise control of stoichiometry, homogeneity and purity. We have been using combustion synthesis for many years to obtain different grades of rare earth doped nanoceria for SOFC applications [28–32]. In order to investigate the suitability of ceria doped with oxides of RE-elements, it is of crucial importance to characterize the powders to achieve desirable properties. Powder characteristics such as morphology, crystallite size and its distribution, agglomeration and surface area are dependent on synthesis method and affect strongly the properties of the respective ceramics.

This work describes a systematic study and characterization of some selected rare earth (RE) doped ceria nanopowders such as $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC), $Ce_{0.9}Sm_{0.1}O_{1.95}$ (SDC), $Ce_{0.9}Er_{0.1}O_{1.95}$ (EDC), $Ce_{0.9}Pr_{0.1}O_{1.95}$ (PDC), $Ce_{0.9}Nd_{0.1}O_{1.95}$ (NDC) and $Ce_{0.9}Y_{0.1}O_{1.95}$ (YDC) prepared via citric acid–nitrate combustion reaction. The aim of present work is to investigate the influence of dopant on the structural characteristics of nanoceria.

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2. Experimental

2.1. Combustion synthesis

Nitrate–fuel combustion method was applied to prepare rare earth-doped ceria (RE-doped ceria) powders with a chemical composition of $Ce_{1-x}RE_xO_{2-x/2}$, where RE: Gd, Sm, Er, Pr, Nd and Y and the concentration of all dopants was maintained constant at 10 mol%, (X: 0.1).

Stoichiometric amounts of cerium, gadolinium, samarium, yttrium, praseodymium and neodimium-nitrate hexahydrates and erbium-nitrate pentahydrates (all nitrates are from Sigma-Aldrich, high purity ≥99.9%) were considered as starting materials. Cerium-nitrate and the corresponding amount of each RE-nitrate were dissolved in distilled water and each resulted solution was stirred to form homogeneous mixed solution. The required amount of anhydrous citric acid (ACS reagent ≥99.5%) as the organic fuel, calculated from the basic principle of propellant chemistry for each dopant [33], was also dissolved in each homogenized nitrate solution. Each reaction mixture was transferred into alumina crucible (100 ml) and inserted in a preheated muffle furnace at 500 °C. The spontaneous reaction started as the solution reached the point of combustion which led to burn vigorously. As a consequence of combustion reaction, a porous solid foam was finally obtained and converted into powder by simple grinding. The as-synthesized RE-doped ceria powders were calcined at 700 °C for 2 h to achieve fully crystalline structures.

2.2. Characterization

The thermal analysis of as-synthesized RE-doped ceria powders was investigated by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) using a Netzsch-STA 449C equipped with a mass spectrometer (Netzech-QMS 403C) for the identification of evolving gasses. The heat flow and weight change of samples placed in Pt crucibles were measured in air (50 ml min^{-1}) from 25 to 1300 °C at a heating rate of 5°C min^{-1}.

The Brunauer–Emmett–Teller (BET) measurement was carried out to obtain the surface area of the as-prepared and calcined powders. The crystalline structure of each as-synthesized and calcined RE-doped ceria powder was analyzed by X-ray diffraction (XRD) 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 per step, over the scan range from 20 to 80°.

Microstructural observations were carried out by scanning electron microscopy (SEM, Philips XL30) and transmission electron microscopy (TEM, JEOL JEM 2000 EX). All samples for TEM 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. Once ethanol was evaporated, the images were recorded using TEM.

3. Results and discussion

The TGA of the all as-synthesized RE-doped ceria powders is presented in Fig. 1 which shows different rate decompositions as single or multiple step processes that started at room temperature. When complete combustion occurs during synthesis, the only gaseous products released are CO_2, N_2 and H_2O. The dissimilar total weight losses of 7 wt.% for the YDC and SDC, 15 wt.% for the EDC and GDC and 27 wt.% for the PDC and NDC are visible.

As it can be seen in Fig. 2, the DTA curves of as-synthesized powders show a broad exothermic reaction that starts around 150 °C. The exothermic reaction for SDC, GDC, NDC and YDC did not occur with any sudden change in weight that can be attributed to the dehydration of water. In the case of PDC at 400 °C and EDC at 150 °C, a sudden change in the weight loss that can be attributed to the evolution of unreacted residues formed during combustion. The change in slope observed at 900 °C for SDC and EDC could be due to the reduction of Ce^{4+} to Ce^{3+} causing chemical expansion at high temperature. In addition, all curves show a sudden and short range endothermic reaction at approximately 1120 to 1180 °C. This change in the kind of thermal process is considered as occurrence of crystallization and structural distortion of ceria which has been also reported in previous works [30,34].

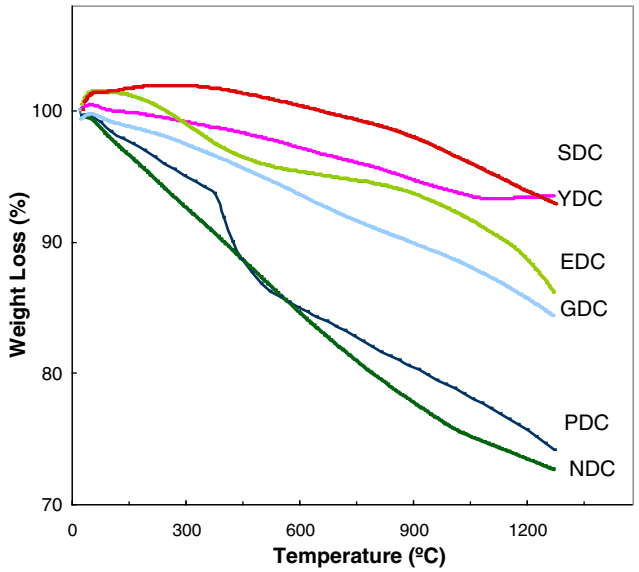

Fig. 1. TGA of as-synthesized $Ce_{0.9}RE_{0.1}O_{1.95}$ (RE = Gd, Sd, Er, Pr, Nd and Y) powders produced by nitrate–fuel combustion method.

Fig. 3 plots the X-ray diffraction patterns of the as-synthesized and calcined RE-doped ceria powders. All samples show single phase with fluorite crystal structure, Fm3m space group [35,36] and all peaks can be assigned to the crystal planes match well with the each RE-oxide composition [30], which shows fully incorporating of the different dopants into the ceria lattice and forming a solid solution of the RE_2O_3–CeO_2 system [13,19]. Comparing the XRD pattern of each as-synthesized and

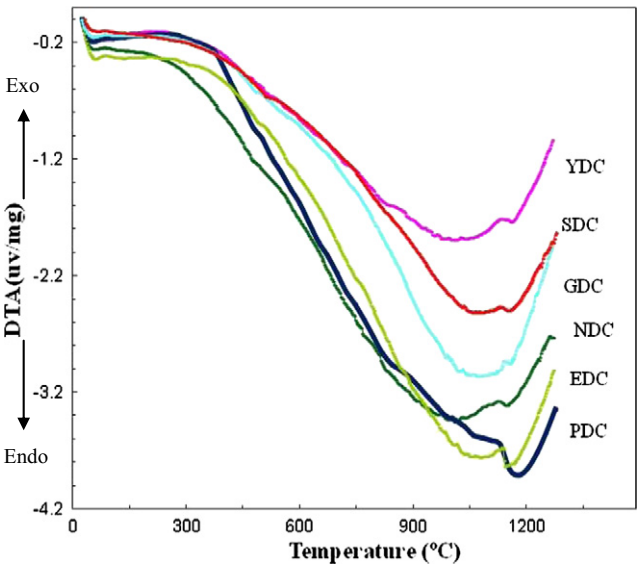

Fig. 2. DTA of $Ce_{0.9}RE_{0.1}O_{1.95}$ calcined powders at 700 °C for 2 h.