

Synthesis and characterization of Gd³⁺ and Sm³⁺ ion doped ceria electrolytes through an *in-situ* sulphated combustion technique

R.V. Mangalaraja^{a,*}, S. Ananthakumar^b, Kasimayan Uma^c, Romel M. Jiménez^d, S.Uthayakumar^e, Marta López^a and Carlos P. Camurri^a

^aDepartment of Materials Engineering, University of Concepción, Concepción, CHILE

^bMaterials and Minerals Division, National Institute for Interdisciplinary Science and Technology (NIIST), Trivandrum, INDIA

^cDepartment of Environmental Technology and Urban Planning, Nagoya Institute of Technology, Nagoya, JAPAN

^dDepartment of Chemical Engineering, University of Concepción, Concepción, CHILE

^eDepartment of Physics, Royal Holloway, University of London, Egham, Surrey TW20 0EX, UNITED KINGDOM

An *in-situ* sulphated-combustion synthesis is reported to obtain gadolinium [Ce_{0.9}Gd_{0.1}O_{1.95}] and samarium [Ce_{0.9}Sm_{0.1}O_{1.95}] doped ceria electrolytes for solid oxide fuel cells (SOFCs). Nitrate precursors of cerium, gadolinium and samarium reactants were mixed homogeneously with a citric acid fuel with an *in-situ* addition of 10 and 20 mol% ammonium sulphate [(NH₄)₂SO₄]. The mixture was combusted at 500 °C and subsequently calcined at 700 °C. The influence of the sulphate addition on the morphology of ceria particles has been analyzed. It is seen that the *in-situ* SO₄²⁻ ions highly favors the nucleation and growth of doped ceria electrolytes on a nanometer scale with an added advantage of improved crystallinity. TEM analysis indicates loosely agglomerated and nearly spherically shaped ceria nano particles with a maximum particle size of 20 nm.

Key words: Combustion, Sulphate ion, Nano ceria, Electrolyte.

Introduction

Conventionally Y₂O₃ doped ZrO₂ is a candidate electrolyte for SOFC's that show an operating temperature of 1000 °C. Presently, the development of a low-temperature SOFC electrolyte is considered seriously in materials research [1-6]. Cerium oxide is a proven solid electrolyte for intermediate operating temperatures (~600-800 °C). Such a high operating temperature gets reduced to below 500 °C when ceria is doped rare earth ions and prepared on a nano scale. Ceria, due to its inherent fluorite structure, exhibits solid solutions readily with divalent and trivalent cations. When rare earth ions such as Gd, Sm, Nd, Y, La, Pr, Ca, Dy, Er, and Yb are doped into ceria, they become partially substituted in the crystal structure of ceria which significantly improves the oxygen ionic conductivity compared to Y₂O₃ stabilized ZrO₂ electrolytes [7]. Depending on the dopant type, the cerium oxide could behave as either an oxygen ionic conductor or an ionic-electronic mixed conductor.

Fine-grained, dense sintered microstructures are essential requirements for separating fuel gas and air at a low operating temperatures. An increased surface exchange and diffusion can be achieved when sintered ceria contains

nano-grains. Ceria nano particles through precipitation, hydrothermal, solvothermal, hydrolysis, pyrolysis, reverse micelle, sonochemical, and sol-gel processes have been attempted for ceria nano particles [5-8]. Although these techniques are seen to be successful on a laboratory scale, due to increased reactivity and high surface area, grain growth is inevitable during further calcination and sintering. A temperature of more than 1300 °C is usually employed to obtain fully-sintered, dense ceria and it is extremely difficult to prevent the grain growth of ceria at this sintering temperature. Gd, and/or Sm doped ceria have been regarded as the most promising electrolytes for intermediate temperature solid oxide fuel cells (IT-SOFC). Therefore increased interest is shown to synthesize Gd³⁺ and Sm³⁺ ion doped ceria nano powders. Techniques such as precipitation [9], co-precipitation [10], citrate [11], hydrothermal [12], sol-gel [13], a conventional solid-state method [13], gel-casting [14], freeze drying [15] and oxalic co-precipitation [16] have already been reported in the literature particularly on Gd³⁺ and Sm³⁺ ion doped ceria.

A combustion process is a recognized direct synthesis route to obtain fine scale ceramic oxides [17, 18]. Since the technique is basically exothermic in nature and involves rapid rate of thermal gradient at the molecular level, fully crystalline products are possible in the end. However, a technical limitation is that it is difficult to obtain specific particle morphology with a controlled particle size. The process ultimately yields highly porous particulate networks containing agglomerated nano clusters. The nature of

*Corresponding author:
Tel : +56-41-2207389
Fax: +56-41-2203391
E-mail: mangal@udec.cl

the cluster sizes and morphologies vary with respect to the types of fuels. Glycine, hydrazine, citric acid are a few common fuels reported for the combustion synthesis. Citric acid combustion is better known as a thermally-induced anionic oxidation-reduction reaction. Preparation of relatively pure metal oxides by pyrolysis of citrate precursors has been known for the past three decades [11, 18]. When citric acid is mixed with the precursor salt solution in specific ratios or concentrations, chelates are formed between metal ions facilitating an atomic scale distribution of ions in a polymer network structure. Heating of this polymerized resin causes breakdown of the polymer network to final charring and produced a solid amorphous precursor material. We have been working on modified combustion synthesis involving SO_4^{2-} ions as secondary fuels and also investigating the role of SO_4^{2-} in deciding the morphologies [19]. Addition of SO_4^{2-} ions has been reported earlier in the simple precipitation of yttria nano particles [20-21]. Also the same was attempted for *in-situ* doping of SO_4^{2-} ions. We extended the study for the combustion synthesis of yttria [22] and found that the addition of SO_4^{2-} ions produced fully-crystalline spherical yttria nanoparticles with an average size of 20 nm [19]. In the present study, we have performed a modified nitrate-fuel combustion process involving an *in-situ* sulphate addition to obtain rare earth doped ceria particles. The morphology, phase purity and particle size have been analyzed and the results are presented.

Experimental

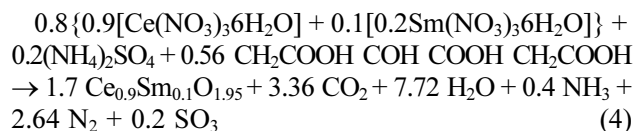
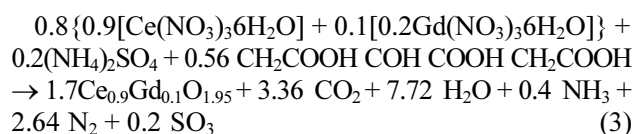
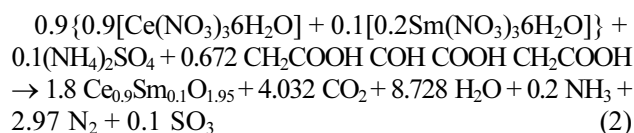
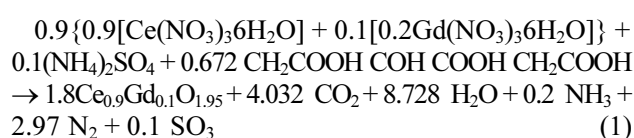
Raw materials

Cerium nitrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, purity 99%], gadolinium nitrate [$\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, purity 99.9%], samarium nitrate [$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, purity 99.9%], ammonium sulphate [$(\text{NH}_4)_2\text{SO}_4$, purity 99.5%] were used as reactants. The chemicals were used in the as-received condition. Citric acid [$\text{CH}_2\text{COOH COH COOH CH}_2\text{COOH}$, purity $\geq 99.5\%$] was used as the fuel. Double distilled water was used as the solvent.

Combustion synthesis

Nitrate salts of cerium, gadolinium and samarium precursors were taken as per the stoichiometry composition of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ and $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$. All the reactants were dissolved in 30 ml of distilled water. After complete dissolution, the citric acid and ammonium sulphate fuels were added. The required amount of citric acid fuel for the complete combustion of the nitrate precursors was determined using the principles of propellant chemistry [17]. In a typical experiment, to synthesize 10 and 20 mol% sulphated rare earth doped ceria 0.672 and 0.56 moles of citric acid were added, respectively. After making a clear homogeneous precursor solution, the reaction mixture was transferred into a platinum crucible (capacity 100 ml). This was inserted into a preheated electric furnace at a temperature of 500 °C for the combustion reaction. The

mixture reached the point of spontaneous combustion in 5 minutes and started burning vigorously. A porous solid foam was finally obtained within 10 minutes. The as-combusted foams were collected and converted into powders by simple grinding. The combustion reaction produced gaseous N_2 , CO_2 , SO_3 , NH_3 and H_2O products. The chemical equations for the combustion process attempted in this study are given in equations (1-4). The chemical reactions (1) and (2) represent 10 mol% ammonium sulphate added gadolinium and samarium doped powders. Similarly, the chemical reactions (3) and (4) represent 20 mol% ammonium sulphate added powders. The $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ and $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$ powders are denoted as GDC and SDC for the gadolinium and samarium doped powders.



The as-prepared rare earth doped ceria powders were calcined at 700 °C for 2 h to obtain fully-crystalline ceria phase [4, 23]. In order to compare, doped ceria was also prepared under identical conditions without any ammonium sulphate addition.

Characterization

As-prepared ceria powders were characterised by thermal analysis (TG/DTA) with a constant heating rate of 10 K·minute⁻¹ (up to 1300 °C) in a He atmosphere using a Netzsch-STA 409 PC/PG analyzer equipped with a mass spectrometer (Balzers MID) to identify the evolved gases. The crystalline nature and phase purity were examined using the powder X-ray diffraction technique (X'Pert Pro, Philips X-ray diffractometer). The X-ray diffraction was recorded using CuK_α radiation. The crystallite sizes were determined using Scherrer's equation [24]. Bulk surface area of the as-prepared and calcined powders were measured by the Brunauer-Emmett-Teller (BET) method in a Micromeritics ASAP 2010 instrument after properly degassing the samples at 120 °C. The morphology, particle size and distribution were analysed by a both scanning electron microscope

(SEM-JEOL 6460 LV) and a transmission electron microscope (TEM-JEOL JEM 2000 EX). TEM samples were prepared by dispersing the powder in dilute ethanol under ultrasonic agitation. A drop of suspension was placed on a carbon coated fine mesh copper grid. Once the ethanol was evaporated, images were seen under TEM.

The samples prepared in the present study are designated as per the addition of dopants (Gd^{3+} , Sm^{3+}) and the amount of ammonium sulphate added. Accordingly the un-calcined samples were designated as GDC, SDC, GDC-10% SO_4 , SDC-10% SO_4 , GDC-20% SO_4 and SDC-20% SO_4 . Similarly the calcined counter parts are designated as GDC-700, SDC-700, GDC-10% SO_4 -700, SDC-10% SO_4 -700, GDC-20% SO_4 -700 and SDC-20% SO_4 -700.

Results and Discussion

Thermal analysis

Thermal decomposition analysis of all the GDC and SDC powders prepared with and without sulphate additions is shown in Fig. 1. A clear difference in the decomposition pattern is seen in the sulphated precursors. Since the reactant mixtures are already exposed to combustion there is no significant weight loss below 200 °C in all the cases. Above this temperature, a gradual weight decrease takes place. The weight loss curves have nearly identical patterns in both the Gd and Sm doped samples. In the unsulphated precursors, the weight loss curves showed no steps and the weight decrease occurred continuously until the peak temperature of 1200 °C. In both the Gd and Sm doped ceria precursors the total weight loss was determined to be close to 15 wt%. The weight decrease is mainly due to the conversion of partially dehydroxylated ceria precursors into fully dehydroxylated rare earth doped ceria powders. Also a significant weight loss is caused by the unburnt carbon existing in the as-prepared precursor mixture. Considering the case of the sulphated precursors,

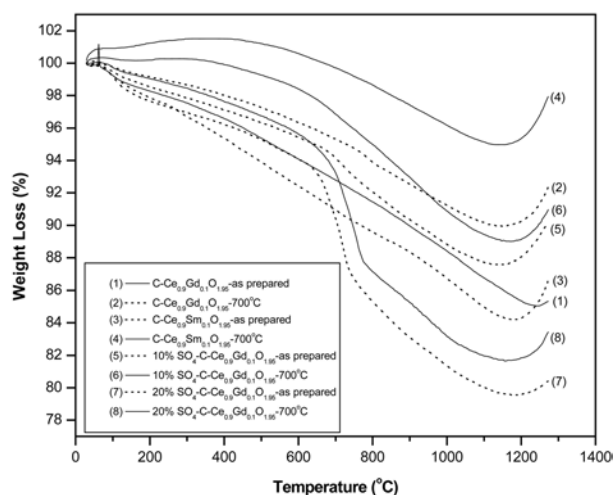


Fig. 1. TGA responses recorded at a constant heating rate of 10 K·minute⁻¹ in a He atmosphere of the nanocrystalline rare earth doped ceria.

as expected the weight loss is higher than for the unsulphated counterparts. In these cases the TG curves showed a narrow decomposition step at temperatures between 680 to 740 °C. This trend is highly prominent in the 20 mol% sulphated precursors. Almost 6% of weight loss was observed at this particular step. This shows that there is a second stage decomposition of ammonium sulphate. Ammonium sulphate is a water soluble crystalline product with a melting point of 235 °C. The theoretical decomposition temperature of ammonium sulphate into ammonia, sulphur trioxide and nitrogenous gas products starts above 280 °C. However, upon thermal treatment the complete decomposition took place above 350 °C. Obviously, the weight loss below 400 °C is caused by the evolution of the gaseous products. Apart from this, the narrow weight loss above 600 °C corresponds to the conversion of amorphous precursor in to a semicrystalline rare earth doped ceria. The TG curves generated for the sulphated samples indicate an added advantage of the presence of ammonium sulphate. In these cases, total weight losses of 13 and 20 wt% were seen respectively for 10 and 20 mol% ammonium sulphate additions. Careful observation of the TG curves obtained for the unsulphated and 10 mol% sulphate added samples, showed that the total weight loss is decreased from 15 to 13 wt% which is very low, indicating that ammonium sulphate contributes as a secondary fuel during combustion reaction. When it is added in excess, the weight loss also exceeds by 5 wt% more than the average weight loss. The total weight loss determined for all the GDC and SDC powders from the TG analysis is shown in Table. 1. Generally, the calcined samples showed a lower weight loss compared to the as-prepared ceria precursors. In the case of the SDC system, the total % weight loss difference is significantly high between the as-prepared and calcined powders. The SDC precursor calcined at 700 °C has shown a weight loss of 5 wt% whereas the as-prepared counterpart showed a weight loss as 15.8 wt%. When we compare these with the GDC powders, the weight loss difference is only 5 wt% between the calcined and as-prepared powders. From Table. 1, it can be seen that the weight loss difference between the as-prepared and calcined powders in the sulphated system is less than 3 wt% irrespective of the

Table 1. Weight loss and gain of the as-prepared and calcined rare earth doped ceria with respect to temperature

Sample	Weight Loss (%)	Weight Gain (%) upto 1275 °C (from ~ 1160 °C)
C-Ce _{0.9} Gd _{0.1} O _{1.95} - as prepared	15	0.3 (from 1240 °C)
C-Ce _{0.9} Gd _{0.1} O _{1.95} -700 °C	10	2.3
C-Ce _{0.9} Sm _{0.1} O _{1.95} - as prepared	15.8	2.8
C-Ce _{0.9} Sm _{0.1} O _{1.95} -700 °C	5	2.9
10% SO ₄ -C-Ce _{0.9} Gd _{0.1} O _{1.95} - as prepared	13.4	2.7
10% SO ₄ -C-Ce _{0.9} Gd _{0.1} O _{1.95} -700 °C	11	2.2
20% SO ₄ -C-Ce _{0.9} Gd _{0.1} O _{1.95} - as prepared	20.4	0.8
20% SO ₄ -C-Ce _{0.9} Gd _{0.1} O _{1.95} -700 °C	18.4	2.0

amounts of sulphate addition confirming and that the presence of *in-situ* sulphate ions enhanced the overall combustion efficiency. In all the cases the TG curves also showed a weight gain between the temperatures 1160-1275 °C and the values are given in Table 1. The values are very close and a marginal difference is seen between the Gd and Sm doped ceria obtained with and without calcination. We are sure that the semi crystalline ceria transformed to fully crystalline at above 1200 °C in all the cases and the doping has not much influenced the structural modification of ceria. Since the oxygen diffusion efficiency is similar in the Gd and Sm doped cerias, the weight increase has not varied apparently. However, in the sulphated counterparts the weight gain is slightly lower indicating its effect. Since the weight gain is an indication of oxygen ionic conductivity of crystalline ceria, the amount of sulphate addition must be strictly controlled.

The results observed in TG analysis are also reflected in the DTA curves which are presented in Fig. 2. In all the cases there exists broad endothermic and exothermic peaks at 380 °C and 1160 °C respectively. As seen earlier, the endothermic peaks at below 400 °C represent the complete decomposition of the unburnt sulphate and citric acid fuels and evolution of the associated gaseous products. The exothermic peaks are confirming the weight gain by the ceria prepared in the present study. Similar to the observations made in the TG analysis, the effect of excess sulphate is also understood from the DTA curves. The sample 20% SO₄-C-Ce_{0.9}Gd_{0.1}O_{1.95} showed an endothermic peak at temperatures 700-800 °C in both as-prepared and calcined powders. This shows that a 20 mol% addition of ammonium sulphate is definitely excessive and will affect the ionic conductivity of rare earth doped ceria. At the same time, the excess sulphate is not observed in the 10 mol% *in-situ* sulphated GDC and SDC powders. Although the as-combusted precursors and calcined powders show a weight gain at 1160 °C the Gd-doped ceria prepared

without a sulphate addition showed only a 0.3% weight gain at 1240 °C. The weight gain has been observed in earlier studies and it is attributed to the effect of the expansion of the cubic ceria crystal structure due to the diffusion of Gd and Sm ions. Since the weight gain took place at 1160 °C, we can confirm that the growth of fully-crystalline ceria possibly occurred at this temperature.

BET

The specific surface areas and primary crystallite sizes for all the GDC and SDC powders prepared in the present study are given in Table 2. Synthesis of rare earth doped ceria is reported already by simple combustion [5, 18, 25-26] and when *in-situ* ammonium sulphate is introduced, the technique produced porous ceria precursor-foams as usual but in this case a considerable difference is seen in the primary crystallite sizes and BET values. As expected, the powders received after combustion showed large surface areas and lower crystallite sizes compared to the calcined powders. In the as-combusted powders, the unsulphated Gd-doped ceria has a higher BET value, 68 m²/g, compared to Sm-doped and sulphated counterparts. In these cases, the BET value is 50 m²/g. Upon calcination an approximately 50% decrease is seen in the specific surface area values and at the same time the crystallite size is increased to double. Specific surface area values indirectly indicate the porous and agglomerated nature of the as-combusted foams and their reactivity. The precursor foams appear to be soft agglomerates containing a mixture of amorphous and semi crystalline doped ceria crystallites. The small crystallite size in the range 12-15 nm confirms the reactivity of the powders. In the sulphated combustion, the powders containing 10 and 20 mol% of ammonium sulphate, the respective specific surface areas are 55 and 50 m²/g. However upon calcination the surface area is decreased to 20 m²/g and the primary crystallite size is sharply increased to 38 and 46 nm. This shows that in sulphated-derived powders, due to the increased reactivity the tendency for particle growth is high which ultimately resulted in an increased crystallite size. The presence of SO₄²⁻ ions was found to be favourable to achieve better crystallinity. Since the crystallite size is comparatively higher in the sulphated ceria this can show how to control the grain growth during

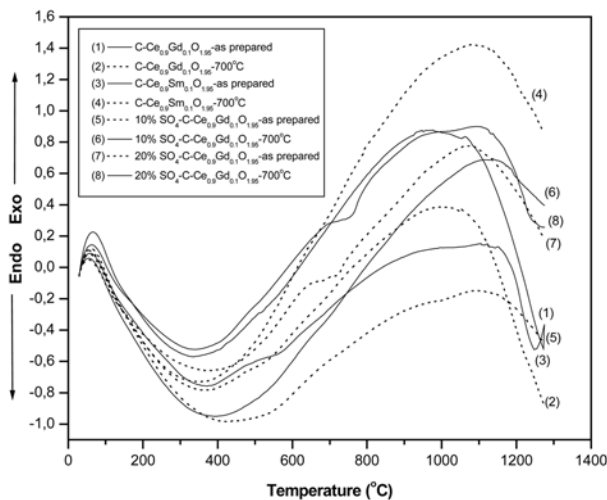


Fig. 2. DTA responses recorded at a constant heating rate of 10 K·minute⁻¹ in a He atmosphere of the nanocrystalline rare earth doped ceria.

Table 2. BET-surface area and primary particle size values of as-prepared and calcined of rare earth doped ceria

Sample	Surface Area (m ² /g)	Primary Particle Size (nm)
C-Ce _{0.9} Gd _{0.1} O _{1.95} - as prepared	68.1	12.3
C-Ce _{0.9} Gd _{0.1} O _{1.95} -700 °C	25.7	32.6
C-Ce _{0.9} Sm _{0.1} O _{1.95} - as prepared	50.9	16.4
C-Ce _{0.9} Sm _{0.1} O _{1.95} -700 °C	36.5	22.9
10% SO ₄ -C-Ce _{0.9} Gd _{0.1} O _{1.95} - as prepared	55.0	15.2
10% SO ₄ -C-Ce _{0.9} Gd _{0.1} O _{1.95} -700 °C	22.0	38.1
20% SO ₄ -C-Ce _{0.9} Gd _{0.1} O _{1.95} - as prepared	50.0	16.8
20% SO ₄ -C-Ce _{0.9} Gd _{0.1} O _{1.95} -700 °C	18.0	46.6

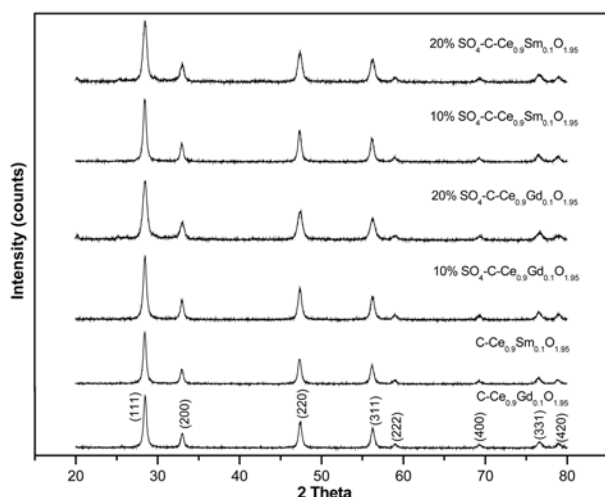


Fig. 3. X-ray diffractograms of the nanocrystalline rare earth doped ceria calcined at 700 °C.

densification. The specific surface area obtained in the present study is significantly higher than the surface area reported earlier for a ceria calcined at 700 °C [18, 23].

X-Ray Diffraction

The powder X-ray diffraction patterns of the as combusted, 10 and 20 mol% ammonium sulphate added and 700 °C calcined GDC and SDC powders are shown in Fig. 3. In all the cases a single-phase cubic fluorite structure of ceria is noticed [JCPDS No. 34-394]. Since there were no peaks representing free Gd and Sm dopants, we can confirm that the Gd^{3+} and Sm^{3+} dopant ions were substituted in the CeO_2 lattice. The crystallinity is also identical for the powders derived through sulphated combustion.

Powder morphology

The morphological features of all the GDC and SDC powders are shown in Fig. 4. The as-combusted powders are generally agglomerates containing platelets and flaky particles. On calcination at 700 °C the TEM images of GDC and SDC powders exhibit spongy nature where flaky crystalline particles are embedded. They also showed pores mainly formed by the fast expulsion of gaseous products during combustion. TEM micrographs further showed that the sulphated powders are comparatively more crystalline than the un-sulphated powders. Also individual grains with no dislocations are observed. From the TEM images the average particle size of ceria derived through sulphated combustion is calculated as 25 nm. In the absence of SO_4^{2-} additions, the crystalline ceria nano-clusters have sharp edges. The addition of SO_4^{2-} resulted in a nearly spherical morphology with loosely agglomerated particles. The TEM images further show that the powders are homogeneous with a narrow particle distribution. The energy dispersive x-ray spectroscopic (EDS) spectra [Fig. 5(a & b)] taken with TEM displays that the ceria particles are phase pure and there is no evidence of SO_4^{2-} impurities present

after calcination. The chemical analysis observed by an EDS attached to the SEM confirmed the chemical composition of ceria calcined at 700 °C for 10 mol% sulphated rare earth doped ceria [Fig. 6(a & b)]. In both the cases, the ceria powders have not shown any sulphate impurities. But in the case of 20 mol% sulphated ceria, it was observed that about 1.5 at% of sulphur is present even after calcination.

Discussion

Citric acid is an α -hydroxy tricarboxylic acid with $-COOH$ and $-OH$ functional groups. The α -hydroxy group acts in combination with one carboxylate group as a complexing ligand to bind the metal cations. Also the melting temperature of citric acid is below 150 °C and it is well established by thermal analysis studies that citric acid decomposes at a temperature 220 °C. During combustion, the metal complex formed by the citric acid fuel undergoes rapid thermo-hydrolysis within a few minutes. At the same time the decomposition of ammonium sulphate also occurs. This generates ammonia gas as well as sulphur trioxide and nitrogenous gases. Release of ammonia gas further accelerates the hydrolysis kinetics. However, the rate of hydrolysis is not consistent due to the exothermic nature of the combustion reaction. The rapid raise in temperature gradients and secondary combustion by the ammonium sulphate additive further inhibit the hydrolysis. Also, in addition to the ammonia gas generation, formation of sulphuric acid and other organic acids such as biuret acid are also expected to form at various intermediate temperatures. This also affects the conversion of the metal complex into a metal hydroxide. Due to such a complex chemical environment, the ceria nuclei formation are considerably retarded leading to a reduced crystallite size. However, the reaction temperature is continuously increasing due to combustion, the CO_2 , SO_3/SO_2 gaseous products start to evolve and at nearly 300 °C no more hydrolysis occurs and the reaction mixture comes completely to the dry state. Since the rate of combustion is unassumingly high [which also happens in a localized manner], the process produces highly porous rare earth doped ceria foams containing soft agglomerates with a semicrystalline or amorphous ceria phase at the end. The evolution of gaseous products also minimizes the heat dissipation, which leads to localized heating [20]. Due to this a nano-clusters with strong inter-particle packing are formed. In the combustion technique, the metal nitrates are impregnated into the polymeric network and later undergo ignition. During cluster formation, depending upon the nature of the additives the crystals attain flaky, plate-like or spherical shapes [27]. Upon calcination the individual particles grow and became well crystalline ceria powders. At high temperature, the flaky and platelets structure break into nano metric spherical particles.

Conclusions

The effect of *in-situ* sulphate additions on the combustion

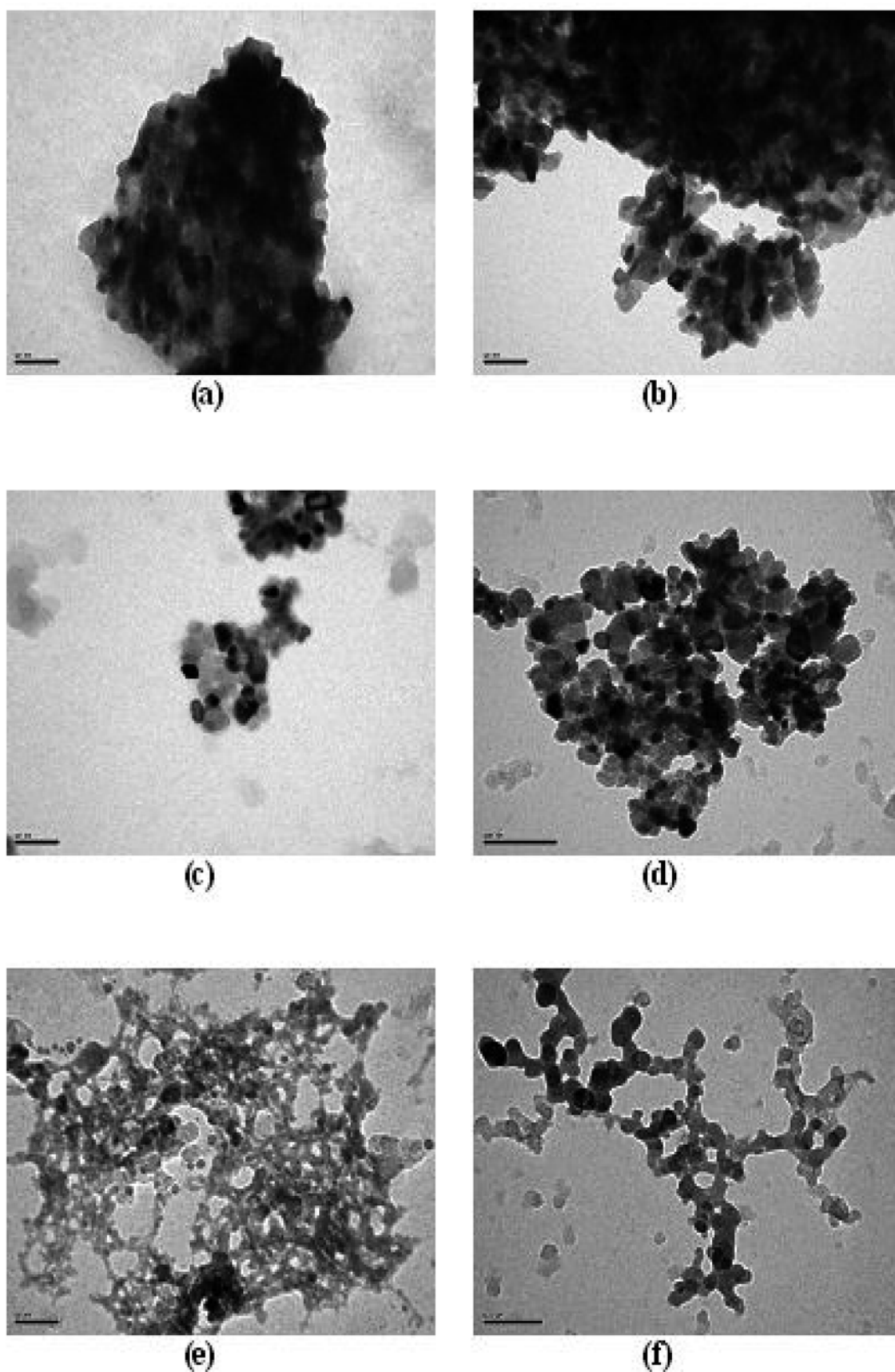


Fig. 4. Transmission electron micrographs of the nanocrystalline rare earth doped cerias calcined at 700 °C (a) C-Ce_{0.9}Gd_{0.1}O_{1.95} -700 °C; (b) C-Ce_{0.9}Sm_{0.1}O_{1.95} -700 °C; (c) 10% SO₄-C-Ce_{0.9}Gd_{0.1}O_{1.95} -700 °C; (d) 10% SO₄-C-Ce_{0.9}Sm_{0.1}O_{1.95} -700 °C; (e) 20% SO₄-C-Ce_{0.9}Gd_{0.1}O_{1.95} -700 °C; (f) 20% SO₄-C-Ce_{0.9}Sm_{0.1}O_{1.95} -700 °C.

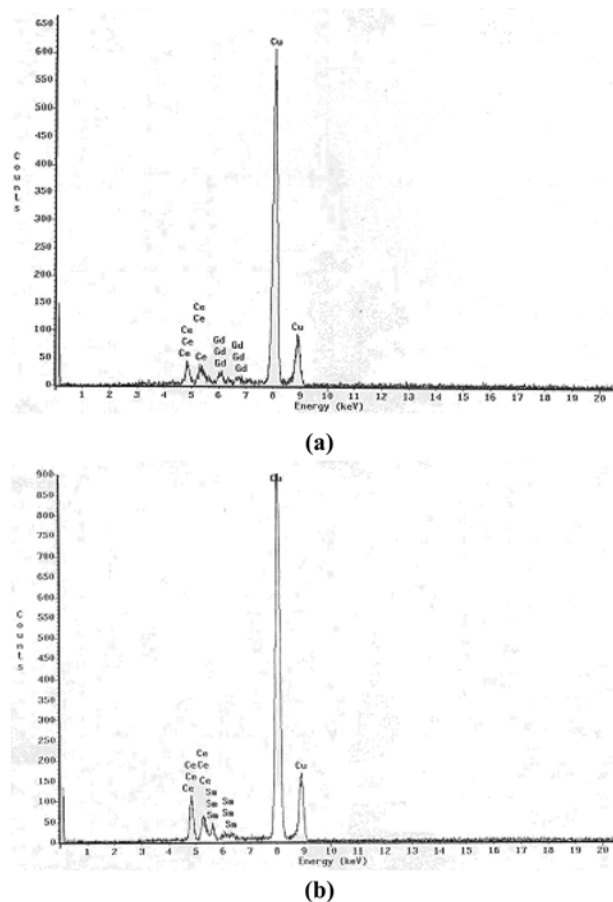


Fig. 5. EDS (attached to the TEM) of nanocrystalline rare earth doped cerias (a) 20% SO_4 -C- $Ce_{0.9}Gd_{0.1}O_{1.95}$ -700 °C; (b) 20% SO_4 -C- $Ce_{0.9}Sm_{0.1}O_{1.95}$ -700 °C.

synthesis of $Ce_{0.9}Gd_{0.1}O_{1.95}$ and $Ce_{0.9}Sm_{0.1}O_{1.95}$ was studied. X-ray powder diffraction analysis confirmed that the combustion synthesis results in a highly crystalline phase pure doped ceria. The *in-situ* addition of ammonium sulphate acts as a secondary fuel and enhances the combustion efficiency. It produced comparatively reactive ceria precursors that can be transformed in to fully-crystalline ceria at 700 °C. The TG analysis showed a comparatively low weight loss in the *in-situ* sulphated precursors indicating that the ammonium sulphate contributes as a secondary fuel for the combustion. A weight gain of < 3% above 1150 °C due to ceria crystal lattice expansion was observed. The weight gain was significantly lower in the sulphated derived cerias. However, the addition of sulphate ions was found to decrease the oxygen ionic conductivity as well as the surface area if it is added in excess. The doped ceria prepared by unsulphated combustion showed a maximum specific surface area of 60 m²/gm which was decreased to ~25 m²/g at 700 °C. The same was true for the Sm^{3+} doped system at 36 m²/g. The primary crystallite sizes ~46 and 30 nm were determined respectively for the doped cerias prepared with and without sulphate additions. Though the sulphated combustion method resulted in a decreased surface area and oxygen ionic conductivity of the doped

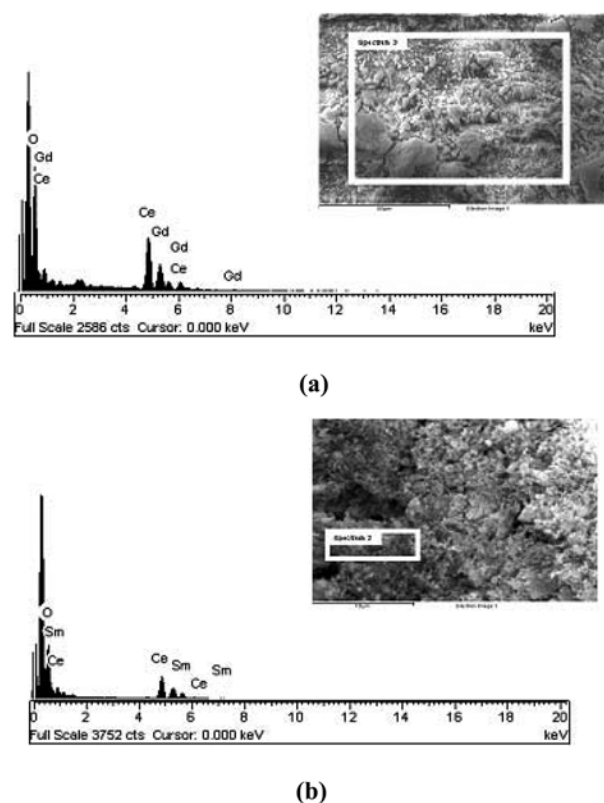


Fig. 6. EDS (attached to the SEM) of nanocrystalline rare earth doped cerias (a) 10% SO_4 -C- $Ce_{0.9}Gd_{0.1}O_{1.95}$ -700 °C; (b) 10% SO_4 -C- $Ce_{0.9}Sm_{0.1}O_{1.95}$ -700 °C.

ceria, the advantages such as enhanced combustion, increased reactivity and generation of nearly spherical ceria particles are encouraging.

Acknowledgement

One of the authors R.V. Mangalaraja would like to thank Direction of Investigation, University of Concepción and FONDECYT (No: 11060302), Govt. of Chile, Santiago for financial assistance.

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