

**Molten Salt Synthesis and Characterization of Doped Ceria Electrolytes**

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**ABSTRACT**

Solid oxide fuel cells (SOFC) are energy conversion devices which convert the energy of chemical reactions directly into electrical energy and heat with high efficiency. Currently a typical SOFC uses yttria stabilized zirconia (YSZ) as the electrolyte due to its outstanding chemical and mechanical properties, and operate at around 1000°C. High operating temperature of YSZ electrolyte can lead to complex material problems like the need of other costly construction materials, interfacial diffusion between electrolyte and electrodes, long term stability etc. Therefore, there was a strong interest in the search for alternative electrolytes which can be used at low temperature operation of SOFC. Doped ceria have been considered as potential candidate for electrolyte material because of their high ionic conductivity and good compatibility with ferritic stainless steels in the intermediate temperature range (600-800°C). Among the various doped ceria compositions investigated so far, Gd and Sm doped ceria are considered most promising. Many methods have been developed for the synthesis of nanocrystalline doped ceria systems. In this work, we are going to present a low temperature synthesis of nanostructured system of ceria doped with Sm, Gd and Nd via a facile and environmental friendly molten salt method. Hydrated metal nitrates and sodium hydroxide are used as the raw materials. The proposed procedure consists of a mechanically induced metathesis reaction and short firing above the melting point of sodium nitrate. The purpose of mechanically induced metathesis reaction is to generate in situ  $\text{NaNO}_3$  flux and to obtain a suitable precursor for the synthesis of target materials in molten nitrates. The prepared materials were then characterized by X-ray diffraction, thermal analysis, infra-red analysis, transmission electron microscopy etc.

**1. Introduction**

A solid oxide fuel cell (SOFC) is considered as a highly efficient power generation system due to its high efficiency, environmental friendship, high waste heat utilization, fuel flexibility etc [1]. A conventional SOFC uses 8 mol% of yttria stabilized zirconia (YSZ) as electrolyte, Strontium doped lanthanum manganite cathode and YSZ-nickel cermet anode. YSZ electrolyte exhibit high oxygen ion conductivity and chemical stability in oxidizing and reducing atmospheres, but its operating temperature is high around 1000°C. The necessity of this high operating temperature has resulted in high cost, physical and chemical degradation of the component materials etc. To be economically competitive, material and fabrication cost should be reduced. One approach to reduce the cost is to reduce the operating temperature so that interconnector, heat exchangers and structural components can be fabricated from

relatively inexpensive materials. Therefore, there is a continuous search for alternate materials which can be used as electrolyte for intermediate temperature (IT) operation in place YSZ [2]. Many studies have been made on various electrolyte materials for the IT-SOFC, such as gadolína dopada ceria, samaria dopada ceria, Scandia estabilizada zirconia, strontium and magnesium co-doped lanthanum gallate. Among these, dopada ceria has been considered as one of the most promising electrolyte materials for intermediate temperature operation of SOFC due to their higher ionic conductivity with respect to dopada zirconia and to their lower cost with respect to lanthanum gallate based materials [3]. The choice of the dopant elements, dopant amount and method of synthesis has a strong influence on the homogeneity and stability of the solid solutions. Among the various dopants studied,  $\text{Gd}^{3+}$  and  $\text{Sm}^{3+}$  singly dopada ceria exhibit better electrical properties [4].

Ceria is a fluorite structured ceramic material (space group  $\text{Fm}\bar{3}\text{m}$ ) that can be readily dopada with a variety of aliovalent (alkaline earth or rare earth) cations to form solid solutions. When so dopada, oxygen vacancies are introduced into the  $\text{CeO}_2$  lattice for charge compensation and the materials become good ionic conductors for a variety of electrical applications. Among the various dopada ceria compositions investigated so far, Gd and Sm dopada ceria are considered as the most promising electrolyte materials for application in solid oxide fuel cells at intermediate temperatures. Conventionally ceria based materials are synthesized at high temperatures. Several other chemical techniques have been adopted for obtaining uniform ultrafine non-agglomerated ceria and dopada ceria particles. They present a higher specific area and can be more easily compacted and sintered than conventional powders. These include hydrothermal synthesis, co-precipitation, decomposition of oxalate precursors, molten salt etc [5-7]. Molten salt synthesis is usually carried out by blending the appropriate precursor chemicals with a large excess of salt and heating the mixture to the reaction temperature, above the latter's melting point.

In this article, we present a novel and simple green chemistry route for the low temperature synthesis of pure and dopada ceria. The proposed two steps methodology combines a metathesis or displacement reaction and a low temperature molten flux. Metathesis or displacement chemical reactions have been extensively used for the very low or even room temperature preparation of a wide range of ultrafine powders of very different nature. Metathesis reaction involves the exchange of atomic/ionic species between reactants, and they proceed almost spontaneously after a short induction period using, for example microwave radiation or mechanical milling. Molten salt fluxes have equally proven to be very useful reaction medium for the rapid- and low temperature synthesis of different multicomponent oxides. Alkali metal nitrates are preferred reaction media because of their low cost, low melting points (for example,  $\text{NaNO}_3=303^\circ\text{C}$ ), high stability over a wide liquid temperature window ( $\sim 550^\circ\text{C}$ ), and high water solubility which facilitates recovery of the target phase by a simple washing step. In this work, we are going to present a low temperature synthesis of nanostructured system of ceria dopada with  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Nd}^{3+}$  via a facile and environmental friendly mechanochemically assisted molten salt method.

## 2. Experimental

Ceria and doped ceria powders were prepared by a two-step method consists a mechanically induced metathesis reaction followed by short firing at temperatures above sodium nitrate's melting point [8]. The starting materials used were high purity (Aldrich, >99+ %) analytical grade Cerium nitrate, Samarium nitrate, Gadolinium nitrate, neodymium nitrate and sodium hydroxide. The nitrates were weighed according to the stoichiometry and mixed with appropriate amount of NaOH, and dry milled together for 30 min in a planetary ball mill by using yttria partially stabilized zirconia (5.2wt%  $Y_2O_3$ ) containers (volume 125 ml) and balls (20mm diameter), balls to powder mass ratio =10:1) at a rotating disc speed of 350 rpm. The amount of the reactant was salt balanced such that there was no alkali metal or nitrate excess. The resulting activated precursor material was dried for 1 h at 120°C to reduce moisture and minimize violent gas evolution on melting. The precursors were then loaded in to alumina crucibles and fired in air for 3 h either at 350 or 500°C using an electrical furnace (Carbolite, heating rate 5°C/min) and cooled thereafter to room temperature. The solidified melt obtained were washed with distilled water to remove the soluble  $NaNO_3$  by product whereas the solid residue was collected by centrifugation. This step was repeated until no traces of  $NO_3^-$  ions were detected by FTIR spectroscopy. The X-ray powder diffraction analysis was carried out to identify the phases at different stages of the synthesis and was carried out by Philips X'Pert diffractometer with Ni filtered  $CuK_\alpha$  radiation ( $\lambda=1.5418\text{\AA}$ ). The crystallite size ( $D_{XRD}$ ) was calculated according to the Scherrer equation

$$D_{XRD} = 0.9\lambda/\beta\cos\theta$$

where  $\lambda$  is the wave length of the radiation,  $\theta$  is the diffraction angle and  $\beta$  is the full width at half maximum. Thermogravimetric and differential thermal analysis were done by using Perkin-Elmer Inc. Pyris Diamond TG/DTA model using a typical sample size of 15mg and heating and cooling rate 5°C/min. Samples were also examined by Scanning electron microscopy in a Philips XL 30 ESEM microscope equipped with an EDAX Inc, energy dispersive X-ray detector for microanalysis. High resolution lattice images and selected area diffraction patterns were obtained using transmission electron microscope (TEM) operating at 300 kV (FEI, Titan 80-300 kV).

## 3. Results and discussion

The exchange of atomic or ionic species between reactant to give stable product is referred as metathesis or displacement chemical reaction. Here we describe the synthesis of doped ceria nanopowders through a simple and cost effective molten salt method, assisted by a mechanically induced metathesis reaction. Molten salt synthesis is usually carried out by mixing the appropriate precursor chemicals with a large excess of salt and heating the mixture to the reaction above the latter's melting point. Most commonly used salt in this synthesis are alkali, alkaline earth metal hydroxides, nitrates, halides, carbonates or sulfates. Nitrates are usually preferred because of their lower melting points (~310°C), their stability is over a wide liquid temperature window (~550°C) and their high water solubility which eases to obtain the sample material by simply washing the solid melt with distilled water. An initial

test has been done of cerium and samarium hydrated nitrates towards producing Sm doped ceria powders in molten  $\text{NaNO}_3$ . Figure 1 shows the X-ray diffraction patterns obtained after firing a mixture of  $0.8\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $0.2\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and commercially available  $3\text{NaNO}_3$  at  $350^\circ\text{C}$  for 3 h. The main reflections present in the spectra are identified as belonging to rhombohedral  $\text{NaNO}_3$ . The most intense peak showing at  $29.40^\circ$  ( $2\theta$ ) is the (104) reflection of this material (JCPDS card No. 36-1474). To ease the discussion, the characteristic X-ray diffraction pattern of rhombohedral  $\text{NaNO}_3$  is also shown at the bottom of the figure. Also some small peaks corresponding to  $\text{Sm}^{3+}$  doped ceria are also visible along with  $\text{NaNO}_3$  reflections.

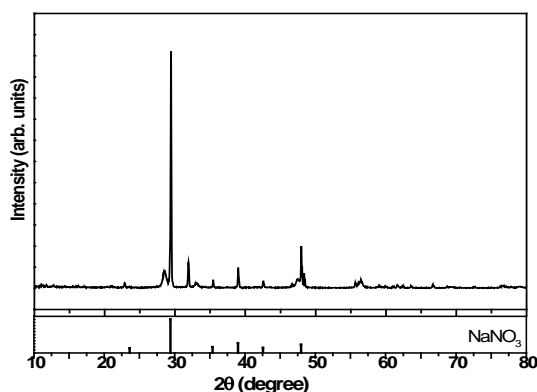


Figure 1. X-ray diffraction patterns of a  $0.8\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $0.2\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $3\text{NaNO}_3$  after firing at  $350^\circ\text{C}$  for 3h

Figure 2 show the X-ray diffraction pattern obtained for the reaction mixture at different stages of experimental procedure, i.e., after milling for 30 min (a), after firing for 3h at  $350^\circ\text{C}$  (b) after washing the latter with distilled water (c), and after firing at  $500^\circ\text{C}$  for 3h and washing (d). Figure 2 (a) shows the reflections of  $\text{NaNO}_3$  crystalline product after the milling step; it is obvious that a mechanically induced metathesis reaction took place in such a short milling time. Thus the most intense reflections of rhombohedral  $\text{NaNO}_3$  are clearly visible (e.g., Miller indexes (104), (006), (113) and (018) at  $29.4$ ,  $38.99$ ,  $47.97$  ( $2\theta$ ) respectively, according to the PDF card 36-1474) confirming that sodium ions displaced ceria from their nitrates on milling and transforming them into a different chemical species. It also shows the presence of some weak peaks of  $\text{NaCO}_3$ , the main reflections of  $\text{NaCO}_3$  is seen at  $30.1$ ,  $37.98$ ,  $39.9$  ( $2\theta$ ) respectively. It also shows the main reflection of ceria at reflections at  $28.55$ ,  $33.08$ ,  $47.47$ ,  $56.33$ ,  $59.08$ ,  $69.4$ ,  $76.69$ ,  $79.07^\circ$  ( $2\theta$ ) respectively (PDF card No.34-0394). The position of the XRD peaks moved slightly towards lower angles when ceria is doped with gadolinium, samarium and neodymium. This is because ionic radius increases in the order ceria ( $0.097\text{nm}$ ) < gadolinium ( $0.1053\text{nm}$ ) < samarium ( $0.1079\text{nm}$ ) < neodymium ( $0.1109\text{nm}$ ). So the substitution of ceria with gadolinium, samarium and neodymium in the lattice of ceria would enlarge the crystal lattice. The inset of the figure shows the peaks shift towards lower angles with increase in ionic size. Table 1

show the crystalline size calculated from the full width at half maximum (FWHM) of diffraction peak according to Scherrer equation [9]. Crystalline size obtained in the range 20-28 nm for ceria and doped ceria systems.

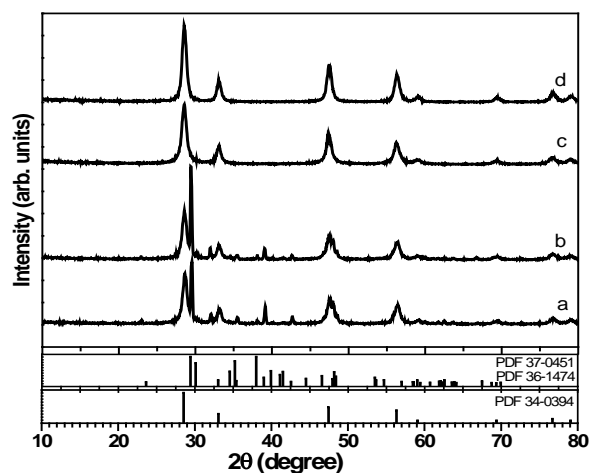


Figure 2. X-ray diffraction patterns of a mixture of cerium nitrate hexahydrate and sodium hydroxide obtained after milling for 30 min (a), firing at 350°C (b) after washing with distilled water (c), firing at 500°C and washed (d).

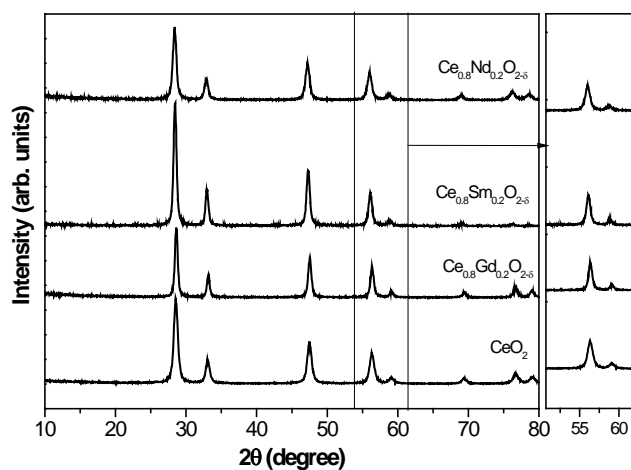


Figure 3. X-ray diffraction patterns of  $\text{CeO}_2$ ,  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ ,  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ ,  $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{2-\delta}$  after firing at 350°C and washed.

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Table 1 –Crystallite size determined by Scherrer equations of the synthesized materials calcined at 500°C

$\text{CeO}_2$	20.45nm
$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$	28.39nm
$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$	28.78 nm
$\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{2-\delta}$	23.48nm

Additional confirmation of the metathesis reaction and subsequent  $\text{NaNO}_3$  formation are inferred from the thermal analysis studies. Figure 4 shows the thermal analysis of the  $\text{Sm}^{3+}$  doped  $\text{CeO}_2$  precursor material obtained after the milling step. Differential thermal analysis (DTA) curve shows an intense endothermic event without associated

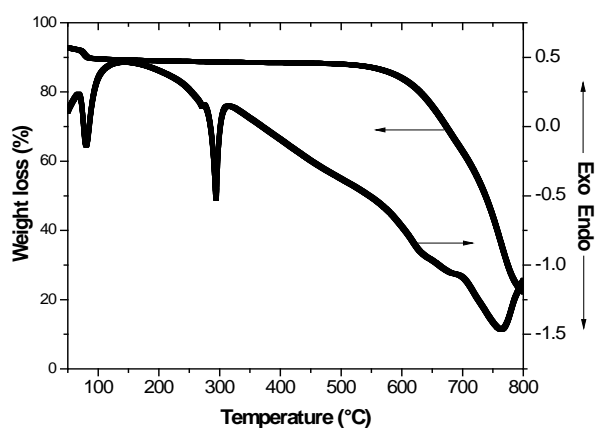


Figure 4. Thermal analysis of the precursor material obtained after milling

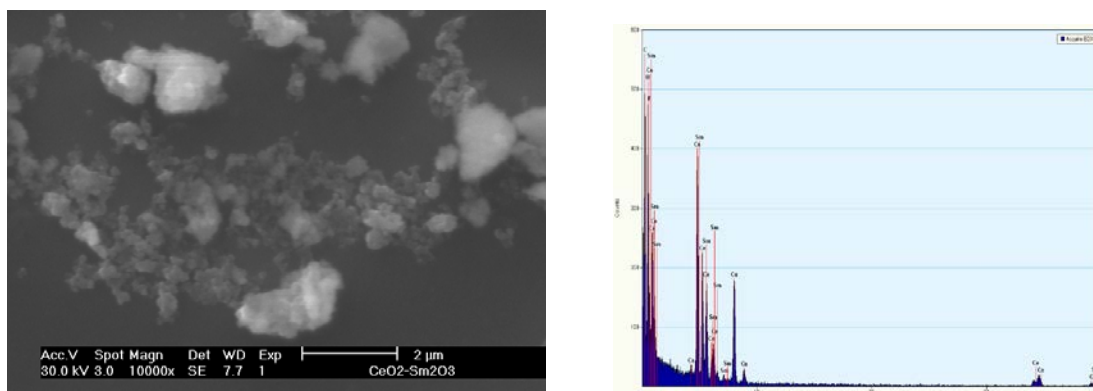


Figure 5. Scanning electron micrographs and EDS analysis of  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$  synthesized powders

weight loss at that temperature at around 301°C, very close to  $\text{NaNO}_3$ 's melting point. It supports the idea of milling induced metathesis reaction. Another endothermic event without associated weight loss observed at 267°C is ascribed to a  $\text{NaNO}_3$  reversible polymorphic transformation from the room temperature and atmospheric pressure stable rhombohedral ordered form (form II) to a disordered phase (form I) [10]. Thermogravimetric analysis showed a small weight loss (~5%) between room temperature and the  $\text{NaNO}_3$ 's melting point.

Table 2 – Chemical composition of the  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$

Element	Wt %	At %
O K	3.16	15.85
CeL	73.79	65.17
SmL	23.05	18.97

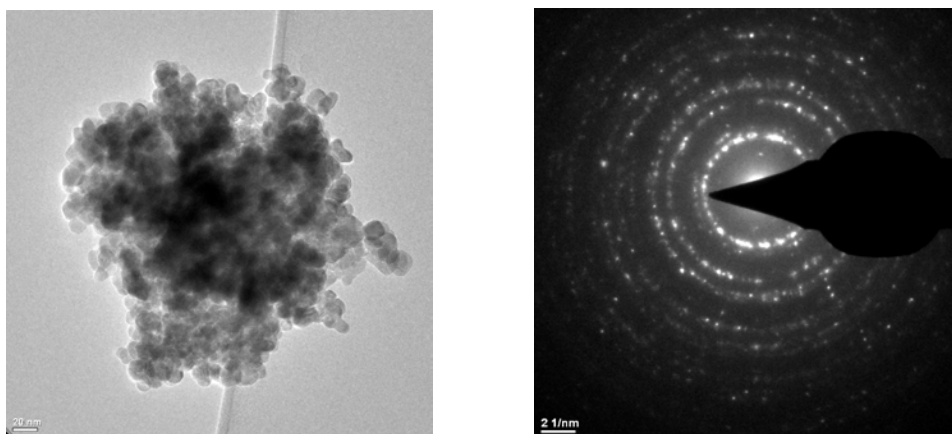


Figure 6. Transmission electron microscopy images of  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$  synthesized powders

Figure 5 shows the scanning electron micrographs of the synthesized powders and the chemical composition of the sample from EDS analysis is shown in Table 2. It shows agglomerate particles of uniform size. The morphology of the sample was studied by TEM and is shown in Figure 6 for the Sm doped ceria. The transmission electron microscopic image show agglomerate of Sm doped ceria sample, and the selected area electron diffraction (SAED) pattern shows highly crystalline behavior. The particle size obtained is of the order of 20nm.

#### **4. Conclusions**

In this work, we have shown that ceria and ceria doped with  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Nd}^{3+}$  nanopowders have been synthesized at very low temperatures ( $350^{\circ}\text{C}$ ) by combining a solid state metathesis reaction and the molten sodium nitrate as reaction media. The X-ray diffraction patterns of all the synthesized samples confirm the cubic fluorite structure after milling for 30min and firing at  $350^{\circ}\text{C}$  and washing with distilled water. The crystal size of the synthesized powders obtained from the XRD analysis is of the order of 20-28 nm. TEM analysis showed the synthesized powders are agglomerate particles of 20 nm size. Further studies and experiments are being done to understand the sintering behavior of these particles.

#### **5. Acknowledgements**

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