

Synthesis and Characterization of Sm³⁺ Doped CeO₂ Nanoparticles

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CERTIFICATE

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This is to certify that the dissertation entitled “***Synthesis & Characterization of Sm³⁺ Doped Ceria Nanoparticles***” being submitted by **Soumyashree Dhal** to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by her under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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Date:

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Rourkela

Date:

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TABLE OF CONTENTS

CONTENTS	PAGE
CERTIFICATE	2
ACKNOWLEDGEMENTS	3
ABSTRACT	5
CHAPTER 1 INTRODUCTION	
1.1. General Introduction	6
1.2. Objective of present work	7
CHAPTER 2 EXPERIMENTAL PROCEDURES & MEASUREMENTS	
2.1. Experimental procedure	7
2.2 Characterization	
2.2.1. DSC-TGA curve	8
2.2.2. X-Ray Diffraction studies	8
2.2.3. IR Spectra	9
2.2.4. SEM	9
2.2.5. BET surface area	9
CHAPTER-III : RESULTS AND DISCUSSION	10
CHAPTER-V: SUMMARY AND CONCLUSION	14
REFERENCES	14

ABSTRACT

Samaria-doped ceria powders were prepared with varying doping concentrations (0.05, 0.5, 1.0, and 2.0). The nanopowders were synthesized using inorganic salts of cerium ammonium nitrate and samarium nitrate. Cerium ammonium nitrate was used as the precursor for ceria and samarium nitrate as the precursor for Sm^{3+} . Dodecylamine was used as surfactant. The characteristics of the sample were investigated by X-ray diffraction studies, DSC-TG analysis, UV, IR, SEM images and BET surface area measurement. From the thermal studies the mass loss was found to be 16 %. XRD data showed the as-prepared sample has cubic fluorite structure and the broad peaks implied that the crystallite size is small (~ 8 nm). 2 mol% Sm^{3+} doped CeO_2 sample heated at 500°C possesses high BET surface area of $75 \text{ m}^2/\text{g}$. FT-IR results showed that the nanopowders heated at 500°C was free from surfactant.

INTRODUCTION

1.1. GENERAL INTRODUCTION

Ceria (CeO_2) is a material of exceptional technological importance due to its unique and versatile properties, which include high mechanical strength, oxygen ion conductivity and oxygen storage capacity and as the basic component of materials for solid oxide fuel cells, sensors, catalysts, and abrasive pastes.¹⁻⁴ CeO_2 containing materials have been profusely investigated in the field of ceramics, catalysis, metallurgy, and smart glass materials.^{6,7} and has also attracted intense interest in electrochemistry and optics.^{8,9}

Ceria is a rare earth metal oxide and is extensively used due to its oxygen storage capacity (OSC), electronic conductivity and oxygen deficiency.¹⁰ Ceria has a wide range of application ranging from heterogeneous catalysis, such as TWCs for automobile exhaust gas emission control, removal of SO_x - NO_x from fluid catalytic cracking flue gases to catalysts for various oxidation and hydrogenation reactions.^{11,12} It is one of the most promising electrolyte materials for SOFC.¹³

Pure CeO_2 has low thermal resistance and low textural stability, which are not high enough to meet the requirements of high-temperature applications such as TWCs.^{14,15} Hence pure ceria is generally not preferred. Moreover the catalytic efficiency may also be reduced at elevated temperatures because of sintering and loss of surface area.¹⁶ This loss in surface area may be attributed to changes in the pore structure and to crystallite growth. Hence it is very much important to improve its textural stability. Doped ceria possess high ionic-electronic conductivity even at relatively low temperatures. The host lattice of ceria is compatible with a wide range of rare-earth ion substitutions.¹⁷

Stabilization of ceria by samarium offers many advantages rather than pure ceria. Among the ceria solid electrolytes, samarium-doped ceria was found to have the highest ionic conductivity.¹⁸ Its enhanced thermal conductivity can be attributed to increase in the grain boundary or interface which increases the concentration of mobile defects in the space charge zone.

1.2. Objective of present work

- Synthesis of Sm^{3+} doped CeO_2 nanomaterials using inorganic precursors and dodecylamine (DDA) as a surfactant.
- Effect of temperature on crystalline size of Sm^{3+} doped CeO_2 nanomaterials.
- Structural characterization using TG, XRD, UV, IR, SEM and BET analysis.

CHAPTER-II

EXPERIMENTAL PROCEDURES & MEASUREMENTS

2.1. Experimental Procedures

Here, the starting materials are ammonium ceric nitrate and samarium nitrate. Separate solutions of both these compounds are prepared in water. These two solutions are mixed with stirring. DDA solution was added slowly with stirring. The obtained solution was stirred and NH_4OH solution was added drop wise to get the precipitate. It was then filtered and washed, dried on the water bath and powdered. The powder was calcined at different temperatures. For comparison the same procedure was followed to prepare samples without surfactant.

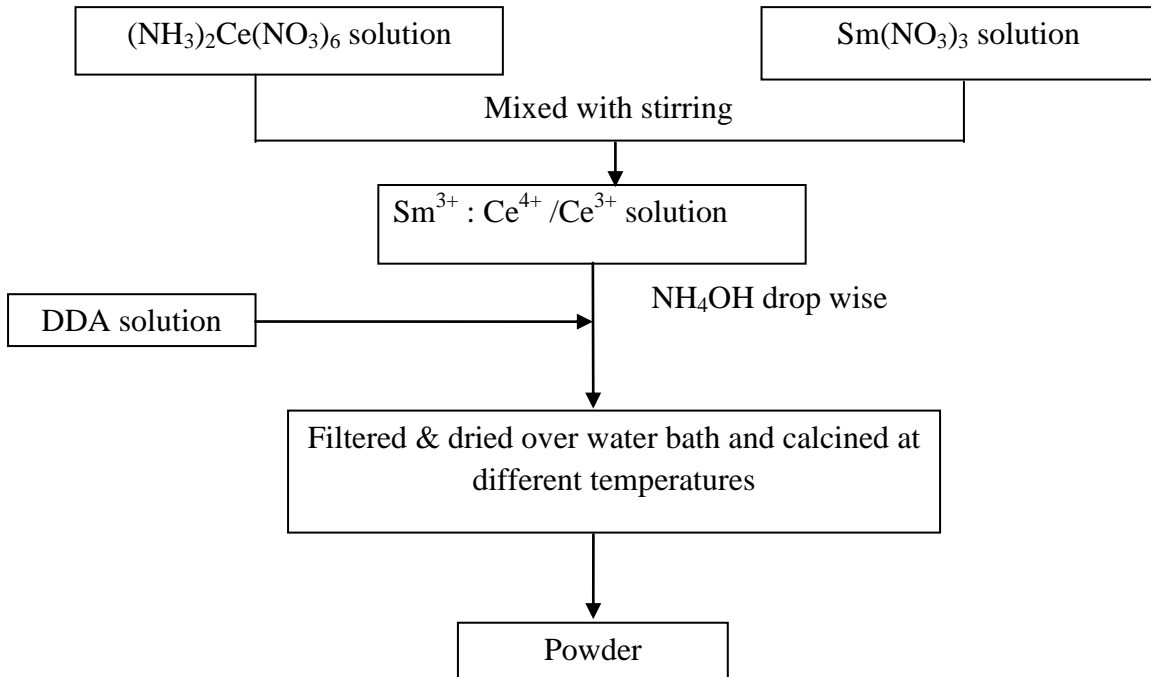


Fig. 2.1. Schematic diagram for synthesis of Sm^{3+} doped CeO_2 powder.

2.2. Characterization and Measurements

Formation of Sm³⁺ doped CeO₂ nanopowder was analyzed using their X-ray diffraction, IR spectra, and SEM analysis.

2.2.1. DSC-TGA curve

Thermal decomposition/combustion of precursor mass into a dried Sm³⁺ doped CeO₂ ceramic powder is studied with thermogravimetry and differential scanning calorimetry (TG-DSC). The data are obtained by heating the sample at 20°C/min. The measurement is done by heating the specimen at a given heating rate in air atmosphere. The peak positions in TG-DSC curve determine thermal decomposition and phase transformation or phase transition temperatures in precursor.

2.2.2. X-Ray Diffraction studies

X-ray Diffraction is used to perform phase analysis. The sample for this measurement was prepared by using a glass slide with a groove as the sample holder. The powder was placed in the groove and was compressed with the help of another glass slide. The excess powder was removed. A very small amount of alcohol was used to paste it properly. The sample at the flat surface at the slide was used to measure its characteristics X-ray diffraction pattern by using X-Ray diffractometer with the following set up,

Target - CuK α of wavelength $\lambda = 0.1540$ nm

Range of diffraction angle - 2θ (20⁰-80⁰)

Scanning speed - 0.08⁰/s

For a crystalline solid, the structure may be specific in terms of crystal unit cell & translations symmetry, the lattice leading to sharp Bragg peaks which are characteristic of the diffraction pattern of the crystalline solids, the structure of the amorphous solid, on the other hand, is characterized by a lack of symmetry, periodicity & long range order, resulting in a diffraction pattern. By using the XRD plots & Bragg's law the peaks were identified & subsequently phases were identified. Average crystallite size in the sample has been calculated from peak widths in characteristic diffraction peaks with the Debye- Scherrer's formula.

$$D = k \lambda / \beta \cos \theta$$

Where λ is the wavelength of the X-ray radiation.

K is a constant taken as 0.89.

θ is the diffraction angle

β is the full width at half maximum (fwhm).

2.2.3. IR Spectra

The IR spectrum was measured in the 400 to 4000 cm^{-1} region for sample dispersed in KBr pellets (in 10:90) with IR spectrophotometer.

2.2.4. SEM

SEM measurements were carried out to investigate the detailed morphology, surface roughness and structure of the powders.

2.2.5. BET surface area

BET specific surface areas were measured where all samples were de-gassed at 373 K overnight prior to adsorption.

CHAPTER-III

RESULTS AND DISCUSSION

Figure 3.1 shows the thermal behavior of 0.5 mol% Sm^{3+} doped ceria nanoparticles heated up to 1000°C . The weight loss in the low temperature range (room temperature to 118°C) was due to the removal of water and gave rise to an endothermic peak in the corresponding DSC curve. The weight loss from 118 to 315°C temperature was attributed to the decomposition of precursors. This was supported by the presence of one exothermic peak at 315°C in the DSC curve. Another exothermic peak at 460°C corresponds to the crystallization of ceria nanoparticles. The exothermic peak at 805°C may be due to phase transformation. The total mass loss was found to be 16%.

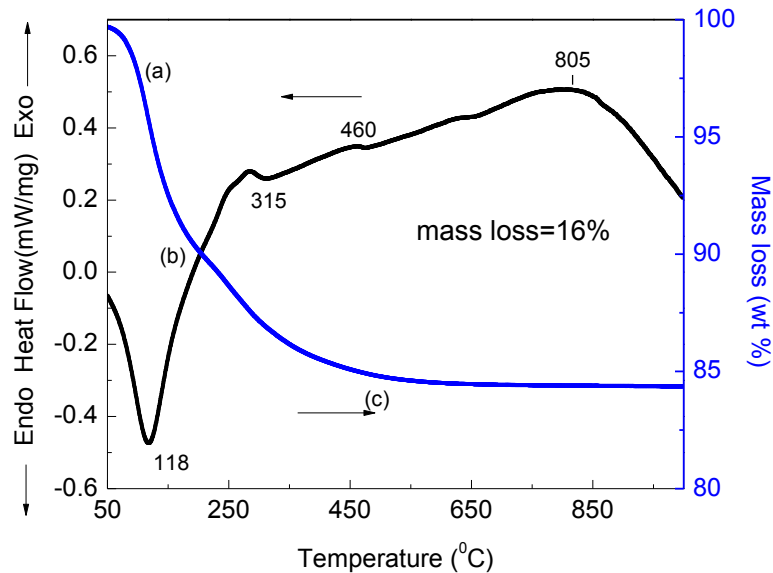


Fig. 3.1. DSC-TGA curve of as prepared 0.5 mol% Sm^{3+} doped ceria.

Figure 3.2 shows the X-ray diffractograms of 0.5SmCeO_2 prepared without surfactant and heated at various temperatures. It shows single phase cubic fluorite structure. All the reflections of cerium (IV) oxide, which is corresponding to the cubic fluorite structure, are observed. It is observed that with increase in calcination temperature the peaks become sharper. This suggests that the crystallite size is increasing with heating at higher temperatures.

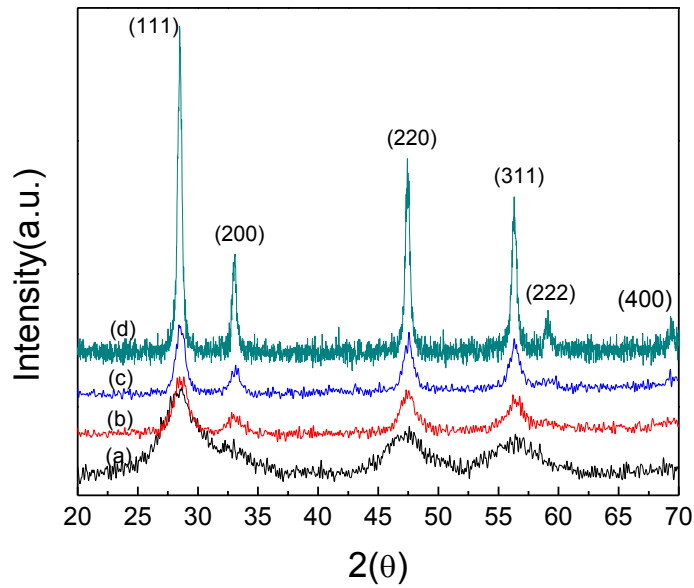


Fig. 3.2. X-ray diffractograms of 0.5 Sm^{3+} doped CeO_2 nanopowders heated at various temperatures (a) asp (b) 500°C (c) 650°C and (d) 800°C .

Figure 3.3 shows the effect of doping on crystallite size. As the concentration of samarium is increased it is observed that the peaks become broader. This suggests that with increase in doping concentration, the crystallite size is decreasing. Hence it can be concluded that samarium also controls the crystallite size.

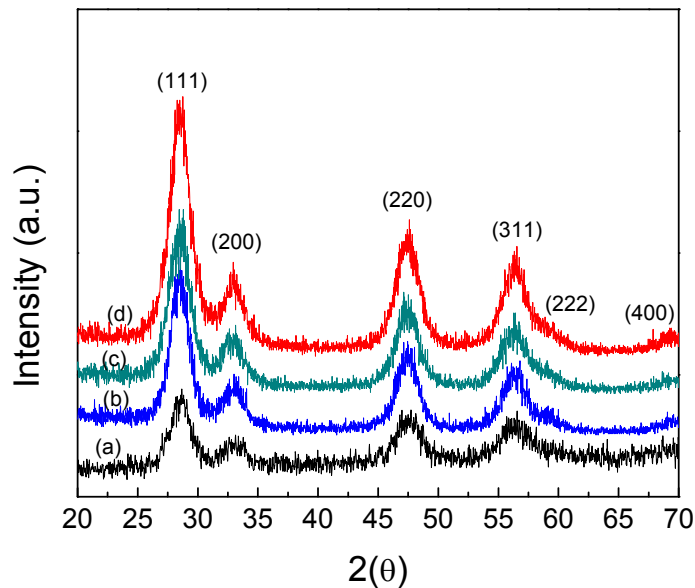


Fig. 3.3. X-ray diffractograms of (a) $0.05\text{Sm}^{3+}\text{CeO}_2\text{-DDA}$, (b) $1.0\text{Sm}^{3+}\text{CeO}_2\text{-DDA}$ (c) $2.0\text{Sm}^{3+}\text{CeO}_2\text{-DDA}$ (d) $0.5\text{Sm}^{3+}\text{CeO}_2\text{-DDA}$ calcined at 500°C .

Figure 3.4 shows the IR spectra of as prepared sample and CeO₂ nanopowders heated at 500°C. Peaks at 962 and 500 cm⁻¹ arise due to Ce-O vibrations. Peak at 1318 cm⁻¹ arise due to Ce-OH deformation. The peaks at 1544 cm⁻¹ correspond to NH stretching and the peak at 2356 cm⁻¹ due to asymmetric stretching of carbon dioxide. The peaks at 2850 cm⁻¹, 2925 cm⁻¹ are due to -C-H stretching of DDA, which are absent in heated samples. So, the powder heated at 500°C is surfactant free. The peak at 3350 cm⁻¹ correspond to OH stretching. For the calcined samples, the peak intensity is decreased compared to as prepared sample. The results demonstrate here that the calcined sample has adsorbed H₂O molecules on the surface of Sm³⁺ doped CeO₂ nanoparticles.

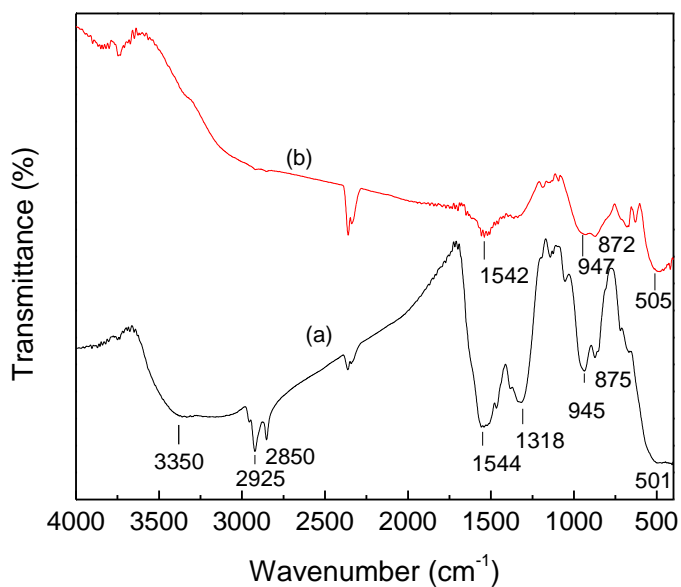


Fig. 3.4. IR spectra of (a) as-prepared 0.5SmCeO₂-DDA and (b) CeO₂ nanopowder calcined at 500°C.

From the SEM images in Fig. 3.5., it is clear that the prepared material is not agglomerated. The particles are not visible clearly. Not much information can be obtained from these images. It requires further investigation by transmission electron microscopy. The BET surface area of $0.5\text{SmCeO}_2\text{-DDA-500}$ was found to be $75\text{ m}^2/\text{g}$, which is found to be greater than the surface area of $0.5\text{SmCeO}_2\text{-500}$ which is $60\text{ m}^2/\text{g}$.

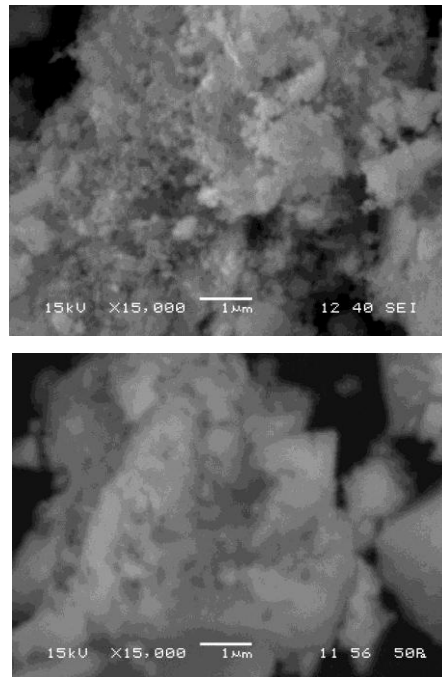


Fig. 3.5. SEM images of (a) $0.5\text{Sm}^{3+}\text{CeO}_2\text{-DDA-500}$ and (b) $0.5\text{Sm}^{3+}\text{CeO}_2\text{-500}$.

CHAPTER-IV

SUMMARY AND CONCLUSION

- Sm³⁺ doped CeO₂ nanopowders were synthesized using inorganic salts of cerium and samarium.
- FTIR results show that Sm³⁺ doped CeO₂ nanopowders heated at 500°C is free from surfactant.
- The crystal structures of all the samples were fluorite type ceria based solid solutions.

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