Synthesis, kinetics and sintering studies of nano/micro CeO₂ powder

Maryam Tavafoghi Jahromi

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SYNTHESIS, KINETICS AND SINTERING STUDIES OF NANO/MICRO CeO₂ POWDER

MARYAM TAVAFOGHI JAHROMI

School of Mechanical and Aerospace Engineering

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Engineering

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ABSTRACT

Fine structured ceria, CeO_2 plays a potential role in a large variety of applications, such as an electrolyte material of solid oxide fuel cell, a catalyst, an optical additive, polisher, and biomedical applications.

There have been a few works on the preparation of nano ceria powder via HMT- $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ system (using HMT as a precipitant and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as a reactant salt). In comparison with the other homogeneous precipitation systems, using HMT- $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ system results in the production of nano ceria powder with finer particle size and narrower particle size distribution, which would result in better electrical and biomedical efficiency of ceria, and also improve sinterability of the synthesized powder.

The first part of this work investigates the production of nano ceria powder via HMT- $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ system and studies the effects of various parameters to control the particle size, size distribution, and morphology of the synthesized powder. As the understanding of crystal growth kinetics is fundamental to control the various properties of nano powder, this work also studies the kinetics and particle growth mechanism of synthesized nano ceria powder. It was observed that, increase in reaction time and reaction temperature resulted in larger particle sizes and higher yield percentages. Different particle sizes of 8.5 to 68.2 nm were produced under various experimental conditions. An acceptable yield of 81% was obtained with a reaction temperature of 90°C for 96 hr. Increase of HMT concentration initially increased the particle size obtained before decreasing it, whereas the increase of cerium nitrate concentration consistently increased the particle size monotonically. It was observed that with the increase of reactants concentration, the grain growth mechanism changed from Ostwald ripening to an

oriented attachment mechanism. More spherical particles were also obtained with the increase of both HMT and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ concentrations.

Fabricating ceria bulk material with a higher density, but with a smaller grain size will improve mechanical as well as electrical properties of ceria. The second part of this work investigates the sintering behavior of commercial ceria powder, and aims to enhance the sinterability while reducing grain growth by doping various amounts of yttria (Y_2O_3) powder. In general, increase of yttria concentration slightly enhanced sinterability, but significantly suppressed the grain growth of samples. In the optimum condition, high relative densities of 98.50 and 99.99% with the particle sizes of 2.5 and 10.7 μm were obtained for the 0.5 mol% and 1.5% Y_2O_3 -doped samples sintered at 1550°C and 1700°C, respectively.

In spite of having higher electrical conductivity, CeO_2 -based materials have weaker mechanical properties compared to their competitors, ZrO_2 -based electrolytes. There have been a few studies on the mechanical properties of ceria obtained via nano indentation technique. In this work, nano/micro indentation properties of undoped and Y_2O_3 -doped CeO_2 are investigated. It was observed that, relative density (ρ) rather than yttria concentration or grain size was the most important factor that affected the mechanical properties of ceria. Increase of density resulted in the higher hardness and elastic modulus, and the lower fracture toughness of samples. In the optimum condition, a fracture toughness of 5.1 $\text{MPa}\cdot\text{m}^{1/2}$, Vickers hardness of 7.7 GPa, nano hardness of 13.0 GPa, and elastic modulus of 371.5 GPa were obtained for the undoped CeO_2 sample ($\rho = 98\%$) sintered at 1700°C.

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Chapter 1: Introduction

Cerium (IV) oxide (CeO₂) or ceria is a pale yellow-white powder. Ceria is a highly refractive ceramic material possessing the cubic fluorite crystal structure (Fig. 1.1) which is stable from room temperature up to its melting point [1-2]. Due to its many distinctive characteristics, such as unique UV absorbing [3], good reactivity [4], and better physical, chemical, and electrical property [5, 6], nano ceria has received much attention in recent years.

Ceria has been exploited to be used in extensive applications, including abrasives of chemical mechanical planarization (CMP) slurry in semiconductor fabrication and polishing material [7-11], catalytic support for automotive exhaust-gas conversion reaction [12-16], oxygen ion conductor in solid oxide fuel cells (SOFCs) [17-23], gas sensor [24-29], and UV absorbent [30, 31]. Recently (2007), some important biomedical applications [32, 33] of nano ceria powder have been also investigated.

Fig. 1.1. (a) Unit cell of the CeO₂ structure. (b-d) the (100) [or (200)], (110), and (111) planes of CeO₂ structure [2].

The present thesis includes two distinct parts. The first part investigates the production of nano ceria powder via homogeneous precipitation method, and the second part studies the sintering behavior and mechanical properties of ceria powder.

1.1. Synthesizing Nano CeO₂ Powder

Over the years many methods, including gas condensation [34], spray pyrolysis [35], reversed micelles (micro emulsion) [36], sonochemical method [37], force hydrolysis method [38, 39], mechanochemical processing [40], and sol-gel method [41, 42] have been proposed to produce CeO₂ particles. Sol-gel processing requires expensive precursor materials, and more complicated reaction mechanism often restricts the potential use of sol-gel method. Using mechanochemical processing, it is difficult to produce ceria powder in the nano ranges, and although micro emulsion is a very efficient method for preparing highly nano dispersed CeO₂, it is difficult to scale up commercially.

Various aqueous-solution based precipitation systems, including ammonia [43-45], ammonium carbonate [46], hydrogen peroxide and ammonia [47], hydrazine [48], hydrazine hydrate [49], oxalic acid [50, 51], urea [52-56], and HMT [57-59] systems have been also used for preparing nanocrystalline ceria-based powders. Audebrand et al [43] used Ce⁴⁺ salts in ammonia solution to produce CeO₂ powder. Using sulfate salt as reactant, they produced strain free particles with a spherical mean shape. However, calcination was necessary to complete the dehydration of complexes and to produce crystalline CeO₂. In 1987, Matijevic et al [52] produced nano ceria powder by aging solutions of cerium nitrate salts and urea at elevated temperatures. Under the best experimental conditions ellipsoidal platelets of oxydicarbonate were crystallized.

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Hirano et al [53] also used urea precipitation system and produced ceria powder with a particle size ranged from 10 to 25 nm. However, using urea as precipitant in both Ce (III) and Ce (IV) systems resulted in production of non spherical particles with cubic or rod like morphology, which did not have good sinterability and were not efficient for the polishing purposes.

In this work, hexamethylenetetramine (HMT) and cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O) homogeneous precipitation system (HMT-Ce(NO₃)₃·6H₂O system) is used to investigate the growth kinetics and particle size of nano ceria. This study extends the original work of using HMT [58, 59] to prepare nano ceria for high yield production, and the crystal perfection is not a major concern. The advantages of HMT-Ce(NO₃)₃·6H₂O system can be summarized as follows:

- i. Using HMT as a precipitant material, very fine particles with a narrow size distribution and good sinterability can be obtained. The key reason is that, the precipitation rate can be controlled through adjusting the hydrolyzing rate of HMT into formaldehyde and ammonia.
- ii. Using HMT-Homogeneous precipitation system, the thermal heat treatment stage or calcination of produced ceria precipitate can be eliminated. Elimination of calcination results in the higher purity, lower agglomeration, and smaller grain size of nano powder [47].
- iii. Fast hydration rate of Ce (III) usually results in the amorphous state of synthesized ceria nano powder. However, nano ceria powder with a good crystallinity can be obtained by using Ce (III) as a reactant salt even when the entire synthesis process is carried out at room temperature [24].

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- iv. Since there is no solid-state decomposition during the processing of nano ceria via homogeneous precipitation, the microstructure of CeO₂ is free from any influence of structural phase transformation, which is priori favorable for obtaining simple microstructure with low strain content [49].
- v. Compared to the other methods, precipitation system is more attractive due to the cheap salt precursors, simple operation, and ease for mass production. Moreover, the reaction conditions of precipitation are mild and adjustable for satisfying a variety of purposes.

There have been some research [43] studying particle growth kinetics of CeO₂ powder produced via ammonia system, but there has not been any report on growth kinetic of nano ceria prepared via HMT- Ce(NO₃)₃.6H₂O system . In this work the growth kinetics of ceria nano particles was also investigated, and a dominant mechanism of particle growth was discussed.

The objectives of the first part of this study can be summarized as follows:

- i. Investigating effects of reaction time, reaction temperature and reactant concentration on particle size and morphology of synthesized nano CeO₂ powder.
- ii. Investigating effects of reactant concentration and reaction temperature on the yield percentage to obtain higher degree of yield in a shorter reaction time.
- iii. Producing more spherical CeO₂ particles for better sinterability and polishing performances.
- iv. Studying particle growth kinetics of CeO₂ powder in order to define the dominant growth mechanism and to yield the growth activation energy.

1.2. Sintering and Mechanical Properties

Cerium oxide-based materials are widely used as the solid electrolyte in the SOFCs. Being a refractory material, CeO₂-based materials are difficult to densify even when sintered at higher temperatures, and increase of sintering temperature in order to approach the full density would result in significant grain growth of ceria samples. According to the literature, increase of grain size would deteriorate the mechanical and electrical properties of ceria material, e.g. considerable results [60-63] are available to show that hardness and fracture toughness of ceramic materials are greater for materials of finer polycrystalline grain sizes. The dependence is often demonstrated on an inverse square root of grain diameter basis as shown for polycrystalline alumina materials. Zhang et al [21] investigated effect of grain size on the grain boundary electrical conductivity (σ_{gb}) of Ga₂O₃-doped CeO₂ (CGO) in SOFCs applications. They reported increase in σ_{gb} with decrease in grain size of ceria samples. The positive effects of smaller grain sizes on enhancement of electrical conductivity and decrease of response time of oxygen gas sensor are also reported by Izu et al [24].

In order to reduce the post-sintering grain size of sintered body, two approaches, either preparing nano powders or using sintering dopants, have been considered. However, nano powders are very expensive, and having a large surface area they cause many difficulties during the processing and sintering stages. For example, nano ceria powder has a very small tapping density, and filling of compaction die in order to fabricate larger and heavier green bodies would be difficult in this case. Moreover, samples produced from nano powder have a very fast shrinkage rate, and are very susceptible to distort or fracture during the sintering steps.

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Many authors [64-69] have investigated the effects of various dopants, such as Mn₂O₃, Fe₂O₃, Gd₂O₃, and Sm₂O₃ on the sintering behavior of ceria. Chen and Chen [70, 71] investigated effects of different alteravalent and aliovalent dopants on the grain boundary mobility of CeO₂ and found that among all of the dopants, Y³⁺ exhibits the most effective suppression of grain growth. Y³⁺-doped ceria is also a serious candidate for variety of high-temperature electrochemical devices [72-75]. However, there have been a few sintering studies [76, 77] on yttria-doped ceria materials. Upadhyaya et al [76] investigated sinterability of yttria-doped ceria powder. In the optimum condition, they could achieve a bulk density of 98% with a grain size of around 6 μm for CeO₂ containing 3 mol% Y₂O₃.

Considering the disadvantageous of nano powder mentioned above, the commercial (micro) ceria powder is used for the sintering studies in the second part of this work. The objective is to enhance the sinterability of ceria powder while restricting grain growth by doping various amounts of yttria powder. It is note worthy that in this study; high temperature calcination of mixed powders is avoided in order to keep yttria as a second phase (not solute) in the ceria matrix. This enables yttria to be more effective to suppress the grain growth of ceria.

Information concerning kinetics of sintering will provide a valuable insight of fundamental basis to control the grain size. However, limited works [66, 78] have been done for understanding the kinetics and sintering mechanism of CeO₂-based materials. Moreover, the kinetics studies mostly have focused on the mechanism of initial or intermediate stage of sintering rather than the final stage of sintering, but the final stage of sintering is considered to be much more important due to the significant grain growth which mostly occurs near the approximately full density. To find out an approach to control the grain size, the present work also investigates the final stage sintering ($\rho \geq 90\%$) and grain growth kinetics of undoped ceria powder.

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The Ceria-based electrolyte has a higher low-temperature electrical conductivity compared to the ZrO₂-based materials, which are most commonly used in the SOFCs applications [79]. However, the ceria-based materials have inferior mechanical properties, and are very susceptible to fail due to thermal stresses and mechanical stresses during fabrication and operation. There have been some studies [79-82] on the mechanical properties of ceria-based materials, but just a few studies on the mechanical properties of ceria obtained via nano indentation technique. In this study the nano indentation properties (nano hardness and elastic modulus), Vickers hardness, and toughness of undoped and Y₂O₃-doped bulk CeO₂ are evaluated. The objective is to reveal the effects of various parameters, such as density, grain size, and yttria doping on the mechanical properties of ceria material obtained via indentation techniques.

The objectives of the second part of this study can be summarized as follows:

- i. Investigating isothermal sintering behavior and post-sintering grain growth of undoped CeO₂ powder.
- ii. Investigating the sintering and grain growth mechanism of undoped CeO₂ powder.
- iii. Enhancing sinterability while restricting the grain growth of CeO₂ samples by doping various amounts of Y₂O₃ powder.
- iv. Investigating effects of Y₂O₃ doping, density and grain size on the nano indentation (nano hardness and Elastic modulus) and micro indentation properties (Vickers hardness and fracture toughness) of CeO₂ samples.

Chapter 2: Literature Review

2.1. Synthesizing CeO₂ Nano Powder via Homogeneous Precipitation Method

In the precipitation procedure, oxide or their precursors are obtained by adding a precipitant (e.g., ammonia, HMT, urea) directly to a solution containing metal ions (e.g., Ce³⁺, Ce⁴⁺). An insoluble salt is precipitated once its solubility limit is exceeded. If dehydrated crystalline CeO₂ is not obtained in the first stage of precipitation, then second stage of precipitation with higher reaction temperatures or calcination will be necessary to complete dehydration.

2.1.1. Effect of Precipitant and Reactant Salt

2.1.1.1. Using Ammonia as Precipitant

Fine powder obtained from the Ce³⁺- ammonia system exhibits lower sinterability in comparison with that from Ce³⁺- HMT system [63], although both powders undergo almost the same chemical reactions during precipitation processing as stated above. This is because the precipitation rate in Ce³⁺- HMT system can be controlled through decomposition of HMT into formaldehyde and ammonia while the precipitation in Ce³⁺- ammonia system is very fast, and there is a little control over the precipitate shape and size because of the rapid change of solution concentration and the discontinuous introduction of precipitant.

Audebrand et al [43] used Ce⁴⁺ salts, namely ceric ammonium and sulfate salts in ammonia solution to produce CeO₂ powder. Using sulfate salts as the reactant material, strain free particles with a spherical mean shape were produced, however calcination

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was necessary to complete dehydration of complexes and produce crystalline CeO₂. He also investigated the kinetics of grain growth in the calcination stage and obtained the apparent activation energy E_a for crystalline growth. The apparent activation energy calculated for ceric ammonium system was greater than that found for ceric sulfate system. The high values of activation energy were found in Nathalie study suggested that the mass-transport mechanism was likely associated with the crystalline-boundary diffusion or lattice diffusion processes.

In 2004, Lee [47] produced nano ceria powder by homogeneous precipitation using a mixture of H₂O₂ as oxidizer and NH₄OH as mineralizer. He reported decrease in particle size of synthesized ceria powder with increase of oxidizer agent concentration.

2.1.1.2. Using Urea as Precipitant

In 1987 Matijevic et al [52] obtained nano ceria powder by aging at elevated temperatures solutions of cerium nitrate salts in the presence of urea. Under the best experimental conditions ellipsoidal platelets of oxydicarbonate crystallized as illustrated in Fig. 2.1. In other situations gel-like precipitates appeared which, in some cases, incorporated either ellipsoidal or rod-like particles. Occasionally tiny spheres were also detected within the gel matrix.

Fig. 2.1. TEM (a) and scanning electron micrograph (SEM) (b) of particles obtained by aging for 2 h at 85°C a solution of 8.4×10^{-3} in Ce(NO₃)₃ and 1.33 moles dm⁻³ in ureanide [52].

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For the urea systems, urea decomposition at the elevated temperature plays an essential role in particle formation. Hydrolysis of urea in aqueous media yields ammonium cyanate or its ionic form [46].

Since decomposition of urea at elevated temperatures is quite slow, reaction 2.1 is a rate limiting step and its rate constant, k , is first order with respect to urea over wide concentration range. In natural solutions the cyanate is converted into carbonate and ammonium ions:

Cerium ion, Ce^{3+} , slightly hydrolyzes in water to form $\text{Ce}(\text{H}_2\text{O})_n^{3+}$, then the precipitation reaction proceeds according to

Finally $\text{CeO}_2(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ changes to cerium oxide, CeO_2 at the higher temperatures in the calcination stage.

Hirano et al [53, 54] also produced ceria using urea as precipitant. Despite Matijevic et al results, they found that, the precipitate formed by heating of the solutions of cerium (IV) salts in the presence of urea was not cerium carbonate but CeO_2 due to the lower basicity and higher charge of Ce^{4+} ions which usually undergo strong hydration and form hydroxide at low pH. The hydrated Ce^{4+} ions would form complexes with H_2O molecules or OH^- ions.

Further polymerization is likely, and both can serve as precursors for the final oxide. In aqueous solution, H_2O as polar molecules tend to take protons away from the hydroxide.

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In this way, Ce⁴⁺ ions precipitate as CeO₂ before reacting with the CO₃²⁻ ions. Hydrothermal treatment at higher temperature promotes the crystallization and crystal growth of CeO₂ from the hydrated CeO₂.n(H₂O) or [Ce(OH)_y(H₂O)_{n-y}]^{(4-y)+}.

Hirano reported that, the crystallinity and particle size of the synthesized ceria decreased with an increase in precipitant concentration. However, this speculation is not in agreement with our results which revealed the existence of maximum point in the particle size versus HMT (precipitant) concentration plot.

From the above literature review it can be concluded that, using urea as precipitant -in both Ce (III) and Ce (IV) systems- results in production of non spherical particles with cubic or rod like morphology which are not desirable for sintering applications. However, HMT-Ce (III) system (as will be discussed in the present work) exhibits better control of morphology, and using this system make it possible to produce hexagonal or nearly spherical particles by appropriate adjustment of experimental parameters.

2.1.1.3. Using Hydrazine as Precipitant

Izu et al [48] investigated the synthesis of nano crystalline particles of cerium oxide at room temperature. They obtained cerium oxide nano powder with a particle size of 10 nm by adding a hydrazine aqueous solution into a cerium nitrate solution. They considered that good crystallinity was attributable to the use of an aqueous solution containing Ce (III) ion as a starting solution.

2.1.1.4. Using Ammonium Carbonate as Precipitant

In 2002 Li et al [46] produced nanocrystalline CeO₂ powder via carbonate precipitation method using ammonium carbonate (AC) as the precipitant and cerium nitrate hexahydrate as the cerium source.

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They showed that the AC/Ce³⁺ molar ratio (R) significantly affects the precursor properties, and spherical nano particles can be produced only in a narrow range of $2 < R \leq 3$. In this method the precursor had an approximate composition of Ce(OH)CO₃·2.5H₂O and crystalline CeO₂ was obtained after calcination of primary precipitate at the higher temperatures.

2.1.1.5. Effect of Different Valences Cerium Salts

Cerium (III) salt usually undergoes three reactions to yield CeO₂ [48].

Reaction (2.6) has a fast reaction rate, while the formation of Ce(OH)₄ from Ce(OH)₃ (reaction 2.7) carrying out under the slow reaction rate. Although the particles form in reaction (2.6) are amorphous, crystallinity could be improved in reaction (2.7) due to the slower rate of Ce(OH)₄ formation from Ce(OH)₃ material.

In the case of Ce (IV), the following reaction occurs:

The direct formation of Ce(OH)₄ from Ce⁴⁺ is carrying out under the fast reaction rate which would result in lower degree of crystallinity of produced nano ceria powder. From the above discussion, it is therefore concluded that, using Ce³⁺ as reactant salt is preferential due to its ability to produce more crystalline nano ceria powder.

2.1.2. Effect of Various Washing Medias

It is generally accepted that the densification behavior and final density depend significantly on the state of agglomeration in powders. The hard agglomeration during sintering prevents complete densification. The agglomeration in aqueous medium involves hydrogen bonding of surface hydroxyl groups on hydroxide precipitates. Once hydrogen-bonded, the water molecule can bridge the surface hydroxide groups on the hydroxide precipitates. During drying and calcining, the hydroxide is converted to the oxide, which forms a solid neck between neighboring precipitates, i.e., a hard agglomerates form as shown in Fig. 2.2 a.

However, the surface properties can be changed using some organic solvents such as alcohol to wash them. It is widely accepted that methanol washing of precipitated gels removed coordinated water and the terminal hydroxyl groups of the gels, and a better powder with little hard agglomeration was obtained. Kaliszewski et al [83] investigated the interaction of ethanol with hydrous ZrO₂ powder and clearly showed that that the formation of surface ethoxy groups rather than hydroxyl groups on alcohol-washed precipitates. Because of steric effects, the ethoxy groups also act to prevent close approach of individual particles. During drying, the removal of ethoxy groups occurs preferentially between neighboring groups on the same powder particles, thus the formation of agglomerates can be avoided. A mechanism proposed by Kaliszewski for ethanol-washed powder is shown in Fig. 2.2 b. This is also helpful for understanding why the nanocrystalline powders obtained from organic mediums usually exhibit a better sinterability than those obtained via aqueous routes.

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Fig. 2.2. Mechanisms proposed by Kaliszewski et al for water-washed (a) and ethanol-washed (b) powders [83].

2.1.3. Effect of Various Solvents

The relationship between particle size (r) and dielectric constant (ϵ) of solution can be shown as [84]

$$\frac{1}{r} = A + \frac{B}{\epsilon} \quad \text{Eq (1.1)}$$

where,

$$A = \frac{kT\rho}{2m\gamma} \ln C, \quad \text{Eq (1.2)}$$

and

$$B = \frac{\rho z + z - e^2}{8\pi m \gamma \epsilon_0 (r_+ + r_-)} \quad \text{Eq (1.3)}$$

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For mixed solvents of homologous alkyl alcohol and water systems, values of A and B can be regarded as constants. Therefore, it is clear that the change in super saturation caused by changing the dielectric constant of mixed solvent can affect the nucleation rate and the particle size remarkably.

For six alcohol/water mixed solvent systems, the dielectric constant varies with nature and composition of the alcohol. As shown in Fig. 2.3, the ϵ value decreases in the following order: EG > MeOH > EtOH > *n*-PrOH > *i*-PrOH > *t*-BuOH. Also, it decreases with increasing the volume percentage of alcohol for these mixed-solvent systems.

It is shown that the particle size of samples obtained in various alcohol/water systems decreased in the following sequence pure water > MeOH/water > EtOH/water > *n*-PrOH/water > *i*-PrOH/water > *t*-BuOH/water > EG/water. All the alcohol except EG obey Eq. (1.1). This is probably due to presence of di-ol characteristics of EG, which is different from other studied alcohol systems. However the true reason is not clear yet.

As expressed in Eq. (1.1), a linear relationship can be obtained between the reciprocal of particle size ($1/d_p$) and the reciprocal of dielectric constant ($1/\epsilon$). As illustrated in Fig. 2.4, it is clearly found that the linear relationship holds approximately, no matter what kind of alcohol is used. However, due to presence of di-ol characteristics the data for EG/water system deviates largely from the linear relationship.

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Fig. 2.3. The dependence of dielectric constant on the composition of different alcohols [84].

Fig. 2.4. The relationship between $1/d_p$ and $1/\epsilon$ for alcohol/water system [84].

2.1.4. Different Kinds of Homogeneous Precipitation Methods

2.1.4.1. Forced Hydrolysis Method

Using forced hydrolysis method, CeO₂ hydrated precipitation can be produced at the elevated temperatures of reaction without using any precipitant materials. However, severe processing condition, such as higher reaction temperature and longer reaction time restrict it to be used in the mass production.

Cerium (IV) ion is less basic than Cerium (III) ion, and its high charge causes strong hydration. The hydrated Ce⁴⁺ ion is readily hydrolyzed to give polymeric species which are intermediate to precipitation of the hydrous oxide. It should then be possible to generate, in principle, uniform ceria particles in situ by kinetically controlled deprotonation of the hydrated Ce⁴⁺ ions at elevated reaction temperatures in the absence of precipitant.

Hsu [38] used different Ce⁴⁺ ions to produce nano ceria precipitation via forced hydrolysis method. He found that the particles morphology could be altered by reactant concentrations and the nature of anion in solution.

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Fig. 2.5 shows effect of concentration of reacting solutions on the natures of precipitated solids. Within the dashed lines the solid phase is formed by homogeneous precipitation due to hydrolysis. Above the upper dashed line solids appear on mixing the reacting components at room temperature, while below the lower dashed line the solutions remain clear even after prolonged aging temperatures up to 100° C. Spherical particles of narrow size distribution were formed at the lower concentrations of ceric sulfate and H₂SO₄ depend on acidity and aging time the particle ranged from 30 to 240 nm.

Hsu also investigated effect of sodium salts on the precipitate formation. Na₂SO₄, NaCl, and NaClO₄ had little effect on average particle size but NaNO₃ caused a decrease in particle diameter. Over a narrow range of intermediate cerium (IV) ion concentration, the addition of Na₂SO₄ generated either single rods or composite rods (Fig. 2.6). The production of these particles in uniform state was extremely sensitive to the working parameters (pH and temperature).

Fig. 2.5. Precipitation domain for solutions containing Ce(SO₄)₂ and H₂SO₄ aged at 90°C for 12 h. Symbols designating different kinds of particles [38].

Fig. 2.6. Electron micrographs of rodlike particles obtained by aging at 90° C for 12 h the solution of $2.5 \times 10^{-3} \text{ mol dm}^{-3}$ in Ce(SO₄)₂, $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ in H₂SO₄ [38].

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2.1.4.2. Sol-Gel Method

The sol-gel process is one of the most promising ways to append functionalities to ceramic materials because of a large number of advantageous that it offers, including a low processing temperature, simplicity of the process and maintenance of excellent control at the molecular level. This process usually consist of two governing reactions involving the hydrolysis and condensation of molecular such as, metal alkoxide to form the oxide network.

Ksapabutr [41] used cerium glycolate complex, as a starting precursor for preparing the ceria materials via sol-gel process. He succeeded in synthesizing high surface area nano ceria particles, however the synthesized powder was porous and highly agglomerated (Fig. 2.7). Among the all variables he studied, hydrolysis ratio ($h = [\text{H}_2\text{O}] / [\text{Ce}]$) was found to be the most important determinant of crystal size and the surface area.

2.1.4.3. Two-Stage Homogeneous Precipitation

Two-Stage precipitation is usually applied in order to satisfy two purposes of a) producing powder with the special morphology, and b) crystallizing precipitated cerium hydroxide gel during second stage with low-temperature hydrothermal treatment. This process is effective to dehydrate the absorbed water and decrease the hydrogen bonding effect leaving a weakly agglomerated powder.

In 2004, Zhang et al [85] developed an economically feasible precipitation method, suitable for a large scale production of ceria oxide powder. For this purpose, two-stage homogeneous precipitation was utilized to produce the cerium hydroxide. In order to avoid agglomeration during drying and calcining, anion surfactant was introduced to solve this problem. They produced the particle size of 30 nm which make the powder suitable for a variety of ceramic forming process.

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Chen [86] produced rod-like particles of CeO₂ by two-stage non-isothermal precipitation, precipitating at 70°C and aging at 0°C temperature. The subsequent aging temperature played an important role on the shape and size of final products. As the aging temperature suddenly reduced to 0°C, the resultant particles retained their original needle-like (Fig. 2.8) structure via the topotactic mechanism, and as rising the temperature above 50°C the products were hexagonal and grown up with increasing temperature via the dissolution-recrystallization mechanism.

Fig. 2.7. Scanning electron micrographs of CeO₂ powders after calcining at 900°C [41].

Fig. 2.8. TEM images of prepared sample aged at 0° C [86].

2.2. Sintering of CeO₂ Powder

CeO₂ is a very useful base material for catalyst supports, electrolytes in SOFCs, and gas sensor. Being a refractory material, ceria requires higher sintering temperatures which would result in significant grain growth and deterioration of mechanical and electrical properties of ceria as a result [21, 60-63]. Over the past years, various approaches, such as using nano powder [78, 87-89], using sintering dopants [64-69, 76, 77, 90-94], and modifying sintering schedule (e.g. two step sintering) [95-101] have been proposed to reduce sintering temperature and post-sintering grain size of ceria as well. The following sections study the effects of mentioned parameters on the sintering behavior of CeO₂ material.

2.2.1. Using CeO₂ Nano Powder

Chen and Chen [57, 87] investigated the micro structure evolution and sinterability of ceria nano powder (particle size = 14.5 nm). In the optimum condition they produced the sample with a nearly full density of 99.99%, and a grain size of 1.46 μm at the sintering temperature of 1300°C. Zhang et al [65] used micro ceria powder (particle size = 0.3 μm), and they could achieve a relative density of 98%, and a grain size of 27 μm at the sintering temperature of around 1650°C. Much lower sintering temperature and the smaller grain size of samples reported by Chen and Chen is, in fact, owing to the nano scale sintered powder which has larger surface area and is much more reactive than micro ceria powder. However, nano powders are very expensive, and having a high surface energy, they cause many difficulties during the processing and sintering stages. For example, nano powders have a very small tapping density, and filling of compaction die in order to fabricate larger green bodies would be difficult in this case. Moreover, samples produced from nano powder have a very

fast shrinkage rate, and they are very susceptible to distort or fracture during the sintering steps.

Chen and Chen [78] investigated the sintering mechanism and grain growth of nano ceria powder. They showed that in the middle region, when the density is between 40 to 65%, the sinterability of nano ceria powder is controlled by coarsening-motivated packing mechanism which is based on an extension of packing model by incorporating grain coarsening. Coarsening of grains under this assumption leads to decrease of pore volume and an increase of packing density. This mechanism can be described by the following equation

$$\left(\frac{R}{R_0}\right)^3 = 1 - (1 - \rho^2)^{\frac{1}{2}} \quad \text{Eq (1.4)}$$

where R is a particle size, R_0 is normalization constant and ρ is a density.

The activation energy of 426 and 445 kJ/mol were obtained for grain growth and densification of ceria in the middle region. They also analyzed the sintering mechanism of region III (60 to 84%) assuming a conventional sintering mechanism, and showed that the grain boundary diffusion is a dominant mechanism of densification. The activation energy implied by this mechanism was 532 KJ/mol.

2.2.2. Effect of Doping on the Sintering Behavior of Ceria Powder

Many authors [64, 65, 67- 69, 91] have investigated the effects of various dopants, such as Fe₂O₃, MnO₂, Gd₂O₃, CoO, and Sm₂O₃ on the sintering behavior of ceria. Zhang et al [65-67] investigated effect of Fe₂O₃ doping on sinterability, grain size, and sintering mechanism of commercial CeO₂ powder. They [67] reveled that, small amount of Fe doping significantly promoted the densification and grain growth of

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CeO₂ ceramic, while Fe₂O₃ doping more than 5 mol% didn't have any significant effect on the relative density, but it sharply decreased the grain size. They [66] also identified that undoped CeO₂ exhibited a volume diffusion controlled sintering, while the sintering of Fe₂O₃-doped samples was dominated by viscous flow mechanism because of the effect of severely under size dopant which would distort the lattice structure. He reported the activation energy of 311 and 315 kJ/mol for early stage sintering of undoped CeO₂ and 0.5 mol% Fe₂O₃-doped CeO₂, respectively.

Zhang et al [64] also studied the sintering behavior of MnO₂-doped ceria. They showed that, Mn doping less than 1 mol% enhanced densification and promoted the grain growth during the final-stage of sintering. For doping level more than 1 mol% the density remained almost unchanged, and the grain size continued increasing. It was, therefore, concluded that the Mn doping was not a good candidate to suppress the grain growth of ceria samples. The same result was obtained in the case of CoO doping [91], but unlike the effect of Mn doping where the grain size of CeO₂ increased with increase of Mn doping level, the grain size remained almost unchanged over the Co doping level of 1 mol%.

Chen and Chen [70, 71] investigated the effects of MgO, CaO, SrO, Sc₂O₃, Y₂b₃, Gd₂O₃, La₂O₃, TiO₂, ZrO₂, and Nb₂O₅ on the grain boundary mobility of dense CeO₂ in the dopant range of 0 to 1%. They revealed that severely undersized dopants (Mg³⁺, Sc³⁺, Ti⁴⁺, and Nb⁵⁺) have a tendency to enhance grain boundary mobility. Among all of dopants, 1% Y³⁺ exhibited the most effective suppression of grain growth, while Mg²⁺ (at 0.1% doping) and Sc³⁺ (>1%) were the most potent grain growth promoter. From the above reviews it can be concluded that severely undersized dopants such as, MgO or Sc₂O₃ may be appropriate sintering aids of ceria powder, but they are not desirable candidate of sintering dopants due to their deficiency to suppress the grain growth of samples.

2.2.3. Effect of Sintering Schedule on the Grain Size of Oxide Ceramics

Modification of thermal cycle provides opportunities to improve the sinterability of powder compacts while suppressing the grain growth. Two-step sintering (Fig. 2.9) is a typical example of modified sintering schedule that promotes densification process at the first stage of sintering while suppressing the grain growth at the final stage. Successful results [95, 97, 99-101] are obtained from two-step sintering of Y₂O₃, Al₂O₃, BiTiO₃, YSZ, and doped-ZnO materials. However, this method is only applicable for materials, which involve higher activation energy of grain-boundary migration than that of grain boundary diffusion itself [98].

Fig.2.9. Two-step sintering temperature program schedule [97].

2.3. Mechanical Properties of CeO₂

Despite higher electrical conductivity, ceria-based materials have much weaker mechanical properties compared to their competitors, ZrO₂-based electrolytes [79], and are very susceptible to fracture due to thermal stresses and mechanical stresses during fabrication and operation. The following sections review hardness, toughness and elastic modulus of ceria-based materials, and aim to find an approach to improve the mechanical properties of ceria.

2.3.1. Nano Indentation Properties of CeO₂

There have been just a few studies on the nano indentation properties of ceria. Wang and Duncan [102-104] investigated effect of reduction treatment on the mechanical properties of ceria obtained via nano indentation techniques. They revealed that the elastic modulus of undoped ceria sharply decreases with exposure to very low oxygen partial pressures due to expansion of Ce-O bond length, and the nano hardness shows a maximum as a function of P_{O₂}, because of opposing effects of both decrease of elastic modulus and dislocation defect interaction.

The nano indentation properties (in the air atmosphere) of ceria and its competitors, yttria-stabilized zirconia (YSZ), are shown in Table 2.1.

Table 2.1. Nano indentation properties of YSZ and CeO₂-based material.

Material	Density %	Grain Size (μm)	Load (mN)	Hardness (GPa)	Modulus (GPa)	Ref.	Remarks
CeO ₂	94	13	5	9.5	270	102	-
4 mol% Y ₂ O ₃ doped ZrO ₂	99.99	-	200	15	210	105	-
10 mol% Y ₂ O ₃ doped ZrO ₂	-	-	1	16.8	281.5	106	(111) direction

2.3.2. Mechanical Properties of CeO_2 -based Materials Obtained from Micro Indentation and Bulk Mechanical Testing Methods

Wang et al [82] investigated effect of reduction treatment on the mechanical properties of ceria. They found that the flexural strength decreases significantly under very low oxygen partial pressure, whereas fracture toughness increases with decrease of oxygen pressure due to the micro crack formation and extension. There have been also some works investigated the effects of various sintering dopants on the mechanical properties of CeO_2 . Ishida [79] investigated effects of Y_2O_3 , Gd_2O_3 , and Sm_2O_3 doping on the mechanical properties of CeO_2 . He concluded that the fracture strength is influenced by the dopant concentration rather than the kind of dopant. Shemilt [81] revealed that fracture toughness of doped ceria is relatively insensitive to the composition of the dopant as well as to the level of doping, and Sato [80] showed that the fracture toughness, fracture strength, and hardness of Y_2O_3 , Gd_2O_3 , and Sm_2O_3 decrease as the dopants content is increased. It is worth mentioning that, these studies have not deeply investigated various effects of doping which can affect mechanical properties under different mechanisms, such as change in relative density and grain size, introduction of oxygen vacancy and etc., and as it is obvious from the above reviews, the conflicting results have been reported in some cases. In this study, the various effects of doping, density, and grain size are investigated individually in order to clarify the reasons behind the improvement or deterioration of mechanical properties with increase of yttria doping.

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Some mechanical properties of CeO₂-based materials and their competitor, yttria-stabilized zirconia (YSZ) obtained from the micro indentation or bulk methods are summarized in Tables 2.2, 2.3, and 2.4. It is known from the literature [107, 108] that the mechanical properties obtained from micro indentation are much lower than the nano indentation owing to the indentation size effect or the larger indentation load applied. In fact, in nano indentation method the weaker micro structure features, such as grain boundaries and defects are not expected to have a significant influence on the mean value of nano hardness due to the smaller indentation sizes.

Table 2.2: Vickers hardness of CeO₂ and ZrO₂-based materials.

Material	Density%	Grain Size (μm)	Vickers Hardness (GPa)	Ref.
CeO ₂	94	-	3.9	109
10 mol% SmO _{1.5} doped CeO ₂	96	-	8.7	81
ZrO ₂	93	-	6.1	110
1Y ₂ O ₃ 6CeO ₂ mol% doped ZrO ₂	99.99	0.17	11.91	111
1.5Y ₂ O ₃ 8CeO ₂ mol% doped ZrO ₂	97	-	9.5	112
3.3 mo% Y ₂ O ₃ doped ZrO ₂	-	-	12.2	113

Table 2.3: Elastic modulus of CeO₂ and ZrO₂-based materials.

Material	Density%	Grain Size (μm)	Elastic Modulus (GPa)	Method	Ref.
CeO ₂			264	Four-point bend testing	82
CeO ₂	99	4.6	175	Small punch method	80
10 mol% Y ₂ O ₃ doped CeO ₂	99	1.80	125	Small punch method	80

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Table 2.4: Fracture toughness of CeO₂ and ZrO₂-based materials.

Material	Density%	Grain Size (μm)	Fracture Toughness (MPa.m ^{1/2})	Method	Ref.
CeO ₂	94	-	1.5	SENB method	109
CeO ₂	95	-	0.95	Chevron notch	82
CeO ₂	99	4.6	1.3	indentation	80
10 mol% Y ₂ O ₃ doped CeO ₂	99	1.80	1.1 5	indentation	80
10 mol% SmO _{1.5} doped CeO ₂	96	-	2.4	indentation	81
1Y ₂ O ₃ 4CeO ₂ mol% doped ZrO ₂	99.99	0.58	13.96	indentation	114
1.5Y ₂ O ₃ 8CeO ₂ mol% doped ZrO ₂	97	-	11	indentation	112
3.3 mol% Y ₂ O ₃ doped ZrO ₂	-	-	10.9	indentation	113

2.4. Applications of Ceria-based Materials

2.4.1. Nano CeO₂ Powder

2.4.1.1. Biomedical Applications

Recently (2007), some important biomedical applications [32, 33] of nano ceria powder have been reported. James McGinnis and co-workers [33] have shown that cerium oxide nano particles can help vision with protection of retina against exposure to damaging levels of light and also assist recovery if injected after exposure. The nano particles protected the cells by scavenging free electrons from the reactive oxygen intermediates which can harm the cells, and rendered them non-reactive. When the nano particles were injected into rat eyes, it was found that pretreated eyes were healthier and more functional than the untreated controls. Moreover, treating the eyes with the nano particles two hours after exposure to the high levels of light rescued retinal function after damage.

2.4.1.2. Catalysis Applications

The main uses of ceria are in the de-pollution of noxious from gaseous steams originating either from stationary or mobile sources. For example, reducibility of CeO₂ facilitates the oxidation of poisonous SO₂ to SO₃ by reacting with SO₂ to give stoichiometric cerium oxide, which is then re-oxidized by oxygen [115]:

Two-way catalyst (TWC) formulation consists primarily of noble metals and metal oxides dispersed either on the surface of alumina pellets or on an alumina wash coat anchored to monolithic ceramic substrate. It is very well-known that the main role of ceria in this complex mixture is to provide oxygen buffering capacity during the rich\lean oscillation of exhaust gases.

A typical closed-loop control system causes the air/fuel ratio (A/F) to cycle rapidly around the stoichiometric composition with a frequency of the order of 1 Hz. Under these conditions, the catalyst is exposed to constantly varying feed stream compositions going alternately from rich exhaust stoichiometry (deficient O₂) to lean stoichiometry (excess O₂). In this environment, ceria has the ability to donate its oxygen for the removal of CO and hydrocarbons (HC) during the oxygen-deficient portion of cycle (R (2.12-14)) while adsorbing and storing oxygen from O₂, NO, and water during excursion into the lean part of cycle (R (2.15-17)). These reactions positively affect the conversation of the three major pollutants (CO, HC and NO) under conditions typically encountered in the normal operation of three-way catalyst,

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2.4.1.3. Polisher

Ceria nano particles are the key abrasive materials for chemical-mechanical planarization of advanced integrated circuit. However, ceria nanoparticles synthesized by existing techniques are irregularly faceted and they scratch the silicon wafers and increase defect concentrations. In 2006 Feng et al [7] developed an approach for synthesis of single-crystal ceria nanospheres, which facilitate precise and reliable mass-manufacturing of chips for nanoelectronics. They doped the ceria system with titanium, using flame temperatures that facilitate crystallization of the ceria yet retain the titania in a molten state. They showed that under these conditions, the inner ceria core evolves in a single-crystal spherical shape without faceting, because throughout the crystallization it is completely encapsulated by a molten 1- to 2-nanometer shell of titania that, in liquid state, minimizes the surface energy (Fig. 2.10).

Fig. 2.10. Microstructure of CeO₂ nanospheres doped with 6% Ti [7].

2.4.2. Solid Ceria-based Material

2.4.2.1. Oxygen Ion Conductor in Solid Oxide Fuel Cells (SOFCs)

Solid oxide fuel cells (SOFC) are energy conversion systems, which convert chemical to electrical energy directly. In essence fuel cells are similar to batteries except that where batteries run down and become depleted; fuel cells are continually replenished with fuel and are able to provide a continuous supply of electric power. Ceria-based films have attracted great interest as electrolyte materials for solid oxide fuel cells operating at intermediate temperatures.

Operating solid oxide fuel cells with doped ceria such as gadolinia doped ceria (CGO) thin films as electrolytes is advantageous due to:

- 1) The high ionic conductivity at intermediate operating temperatures and lower polarization resistance compared to state-of-the-art yttria-stabilized zirconia (YSZ).
 - 2) The possibility to combine low-cost ceramic thin film methods, such as spray pyrolysis, with traditional silicon micromachining technologies
 - 3) The reduction of the ohmic losses through the cell resulting in higher power outputs.
 - 4) Chemical stability of ceria with cathode materials is superior to that of zirconia.
- CGO has been shown to be stable with a wide variety of electrodes, including all the common cathode materials such as LSM, LSC, LSF, LSCF, and LNF.

However, the primary disadvantages of ceria are electronic conduction and reduction at low oxygen partial pressure [18, 19].

Zhang et al [21] investigated effect of grain size on the grain boundary electrical conductivity (σ_{gb}) of impure CGO. They revealed decrease of σ_{gb} with increase of grain size. This can be explained by considering that, most of CGO used in the industrial applications have small amount of SiO₂ impurity (e.g. as a sintering aid), so the σ_{gb} is

dominated by Si-containing grain boundary phases. Increase of grain size results in decrease of grain boundary surface, which leads to increase of SiO₂ density on the grain boundary and decrease of σ_{gb} as a result. It should be considered that for a doped ceria, the grain boundary phases are supposed to be inert, that don't react with or dissolve into the matrix. It means with increase of grain size (annealing temperature) the impurities on the grain boundaries do not dissolve in the matrix, otherwise the two opposite factors of increase of impurity density on grain boundary and dissolution in the matrix will co-operate the grain boundary behavior.

2.4.2.2. Resistive Oxygen Gas Sensor

Using a concentration cells comprising an oxygen-ion conductor have been extensively used as the oxygen gas sensors for automotive exhaust gas. Resistive oxygen gas sensors have a very simple structure, thus allowing for the size to be decreased. TiO₂, SrTiO₃, Ga₂O₃ and CeO₂ are the common materials which are used in the resistive oxygen sensors.

Not only the size factor, but timely response as well is a critical factor for applications of the oxygen gas sensors to automotive exhaust gas. It is important to shorten the response time. The output of the sensor is the resistance of the thick film. Therefore the parameters which affect resistance can also affect response time of sensor.

Izu et al [24] fabricated the resistive oxygen gas sensors based on cerium oxide porous thick film to investigate the effects of changes in grain size and firing temperature on the response time for oxygen gas sensor. They concluded that the response time was depended in principle on the crystallite size, shortening as the crystallite size decreased, and that the response time was unaffected by grain size, if the grain size was the same.

Chapter 3: Thermodynamics of Nano Powder Processing

3.1. Introduction

The crystallization or precipitation of powders involves the nucleation and growth from a supersaturated solution. There are several ways to induce supersaturation in a solution. For the few systems where the solubility decreases with temperature, heating can be used to supersaturate the solution. Elevated pressures can also be used as a mechanism to precipitate a particular crystal phase which may not be stable at atmospheric pressure (e.g., hydrothermal synthesis).

Supersaturation can also be induced by adding another component to the reaction environment, thus reducing the solubility of the solute. Any of these methods may be used to generate a particular solid phase; however, the most common method used in inorganic chemical systems is that of a chemical reaction, which produces an insoluble species. Traditionally, reactive crystallization is referred to as “precipitation”. The level of supersaturation for “reaction induced precipitations” is often very high, resulting in high nucleation rates.

In the following chapter kinetics of homogeneous nucleation, growth mechanism and surface morphology of particles in the saturated solution will be discussed.

3.2. Homogeneous Nucleation in Saturated Solution

The overall free energy, ΔG , of the embryo is the sum of two terms: the free energy due to the formation of a new volume and the free energy due to the new surface created given by [116],

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$$\Delta G = -\left(\frac{V}{V}\right)K_B T \ln(S) + \gamma a \quad \text{Eq (3.1)}$$

where $v (= \beta_v r^3)$ is the volume and $a (= \beta_a r^2)$ is the surface area of the aggregate, V is the molecular volume of the precipitated embryo, S is saturation ratio and γ is the surface free energy per unit area.

The area and volume for any polyhedron can be used to define a generalized particle radius, $r (= 3v/a)$, which is the exact definition of the radius of a sphere (i.e., $\beta_v = 4\pi/3$ and $\beta_a = 4\pi$).

This generalized particle radius can be used to calculate the total free energy of a particle size, r giving

$$\Delta G(r) = \left(\frac{\beta_v r^3}{v}\right)k_B T \ln(S) + \lambda \beta_a r^2 \quad \text{Eq (3.2)}$$

When the saturation ratio, $S < 1.0$, $\Delta G(r)$ is always positive and the formation of a new phase is non-spontaneous. Alternatively, when the saturation ratio, $S > 1.0$, $\Delta G(r)$ has a positive maximum at a critical size, r^* , as shown in Fig. 3.1.

Fig. 3.1. Dependence of nuclear size on Gibbs free energy for different saturation ratio S [116].

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The critical nuclear size, r^* , can be obtained by setting $d\Delta G(r)/dr$, giving

$$r^* = \frac{2\beta_a \gamma v}{3\beta_v k_B T \ln(s)} \quad \text{Eq (3.3)}$$

This critical size corresponds to the maximum of the free-energy curve, where $\Delta G_{\max}$ is given by

$$\Delta G_{\max} = \frac{\gamma \beta_a (r^*)^2}{3} \quad \text{Eq (3.4)}$$

Fig. 3.2 shows how the saturation ratio, S , affects the critical nuclear size, where the standard critical size of nuclei is given by

$$r_{std}^* = \frac{2\beta_a \gamma v}{3\beta_v k_B T} \quad \text{Eq (3.5)}$$

The number density of embryos (i.e., number per unit volume) of size, r , can be shown to be

$$N_e(r) = \left(\frac{1}{v_{sol}}\right) \exp\left(\frac{-\Delta G(r)}{k_B T}\right) \quad \text{Eq (3.6)}$$

where v_{sol} is the molecular volume of the solvent.

Fig. 3.2. Critical nuclear size as a function of saturation ratio [116].

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This embryo size distribution function is presented in Fig. 3.3. The rate at which nuclei of critical size are assembled from an embryo and a molecule can be expressed in terms of the following equilibrium reaction:

where the reaction rate is written as

$$\frac{dN(r^*)}{dt} = k_1 N(\text{molecule}) N(r^* - \text{molecule}) - k_2 N(r^*) \quad \text{Eq (3.7)}$$

and K_1 is the second-order rate constant for the assembly of critical nuclei from an embryo and a molecule and k_2 is the unimolecular rate constant for the splitting off of a molecule from a critical nucleus.

This rate can be approximated by

$$\frac{dN(r^*)}{dt} = \left[k_1 \left(\frac{1}{v_{sol}} \right) - k_2 \right] \left(\frac{1}{v_{sol}} \right) \exp \left(- \frac{\Delta G(r^*)}{k_B T} \right) \quad \text{Eq (3.8)}$$

Fig. 3.3. Embryo size distribution function for various values of the saturation ratio [116].

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The approximation made in Eq. (3.8) is that $N(r^*\text{-molecule}) = N(r^*)$. The difference in the rate constants (i.e., $[k_1 (1/v_{sol}) - k_2]$) can be further simplified by considering this formation step to be limited by the diffusion of molecules in solution to the central nucleation site. This means that the rate-limiting step for the formation of stable nuclei will be the splitting off of a molecule from the critical nucleus. This simplified form for the pre-exponential factor can be written as

$$\left[k_1 \left(\frac{1}{v_{sol}} \right) - k_2 \right] \approx k_2 \approx \left(\frac{k_B T}{h} \right) \exp \left(- \frac{\Delta G_D^*}{k_B T} \right) \quad \text{Eq (3.9)}$$

where h is Planck's constant, k_B is the Boltzmann constant and ΔG_D^* is the activation energy for molecular diffusion. From this simplification, a nucleation rate, J , can be defined as

$$J = \frac{dN(r^*)}{dt} = \left(\frac{k_B T}{h} \right) \exp \left(- \frac{\Delta G_D^*}{k_B T} \right) \times \left\{ \frac{1}{v_{sol}} \exp \left(- \frac{\Delta G(r^*)}{k_B T} \right) \right\} \quad \text{Eq (3.10)}$$

Again, Eq. (3.10) says that the rate of formation of a critical nucleus is limited by the rate at which molecules leave the crystal lattice. The kinetic factors in this equation are of the order of $\sim 10^{35} \text{ cm}^{-3} \text{ s}^{-1}$ for liquids near their boiling points, which is the maximum possible nucleation rate, $J_{\max}$.

An alternative simplifying assumption can be used in defining a nucleation rate by applying Einstein's equation (i.e., $\lambda^2/2t = D$) to identify a reciprocal diffusional time, t^{-1} , and equating that to k_2 , where

$$t^{-1} = \left[k_1 \left(\frac{1}{v_{sol}} \right) - k_2 \right] \approx k_2 \approx \left(\frac{2D}{d^2} \right) \quad \text{Eq (3.11)}$$

where D is the diffusion coefficient of the solute and λ (i.e., the root-mean-squared displacement) is estimated as the molecular diameter, d .

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This estimation of the pre-exponential factor provides us with a much simpler expression for the nucleation rate given by

$$J = \frac{dN(r^*)}{dt} = \left\{ \frac{2D}{d^5} \exp\left(-\frac{\Delta G(r^*)}{k_B T}\right) \right\} \quad \text{Eq (3.12)}$$

The kinetic factor in this equation (i.e., $2D/d^5 = J_{\max}$) is of the order of $\sim 10^{30} \text{ cm}^{-3} \text{ s}^{-1}$ for liquids, which is again the maximum possible nucleation rate. Note that this value is five orders of magnitude lower than the estimate of $J_{\max}$ in Eq. (3.10). However, if we use this simplified expression [i.e., Eq. (3.12)] for the nucleation rate, a generalized plot of the nucleation rate vs the saturation ratio can be generated, as presented in Fig. 3.4. This figure is a log-log plot of the nucleation rate, as described by $J = J_{\max} \exp(-\Delta G(r^*)/k_B T)$, versus the saturation ratio, S . The nucleation rate can be made dimensionless by dividing the nucleation rate by $J_{\max}$ or [more precisely as $(\log S)^{-2} \rightarrow 0$] for different values of A $\{= 4\beta_a^3 \gamma^3 v^2 / [27\beta_v^2 (k_B T \ln(10))^3]\}$. After normalizing, the dimensionless nucleation rate can be rewritten as,

$$\log\left(\frac{J}{J_{\max}}\right) = -A[\log(S)]^{-2} \quad \text{Eq. (3.13)}$$

J : nucleation rate

A : temperature dependent rate constant

S : saturation

From Fig. 3.4, we can see that the nucleation rate increases sharply from a critical value of supersaturation (i.e., $S = S_{\text{cr}}$ given by the intersection of a nucleation curve with the x-intercept), and then asymptotically approaches its maximum value. The critical value of supersaturation, S_{cr} depends on the value of the constant A .

Fig. 3.4. Generalized nucleation rate diagram which describes the homogeneous nucleation rate as a function of the saturation ratio [116].

3.3. Particle Growth Mechanism

In general two mechanisms of Ostwald ripening and oriented attachment (OA) are supposed for the particle growth. In Ostwald ripening mechanism bigger particles grow in the expense of smaller particles, whereas in the OA mechanism smaller particles orientedly attach each other to form bigger particles. Degree of saturation has a significant effect on the particle growth mechanism. At the higher degree of saturation, orientedly attachment of particles is more probable due to the smaller inter-particle distances (the particle growth mechanism will be discussed in details in the subsequent chapters) [116].

The surface morphology of produced nano powder depends on the degree of saturation. In the case of higher solubility (low degree of saturation), atoms prefer dissolving in the solvent rather than clustering and growing, so high amount of the bonding energy is required to add the solute atom to the primary nuclei.

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Since an atom added to the rough surface has several possible sites of attachment with different binding energies (Fig. 3.5), rougher surface is predicted for a higher degree of solubility. In the case of lower solubility the solvent-solvent bonding energy is higher than the solute-solvent one, so atoms easily attach the primary nuclei and cause further growth. A single new atom, added to the rough surfaces can only form a bond with one nearest neighbor, but in the lower degree of solubility this amount of bonding energy is enough for an atom to nuclei on primary surface of particles. As CeO_2 has a low solubility in water, the smooth interface is predicted for ceria particles; this is also confirmed by Feng et al (Fig. 3.6) [7].

Fig. 3.5. Simplistic representation of the solid-solution interface in growing crystal: (a) atomically smooth surface and (b) rough crystal surface [116].

Fig.3.6. Microstructure of CeO_2 nanoparticles. (a) Scanning electron microscopy (SEM) image, (b) low magnification TEM image, and [(c) and (d)] high resolution TEM images of the ceria nanocrystals with faceted shapes. The inset between (a) and (d) is an electron diffraction pattern from the area circled in (b).

Chapter 4: Experimental Procedure

4.1. Nano CeO₂ Powder Processing

4.1.1. Sample Preparation

The CeO₂ nano particles were prepared via a precipitation technique using cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 98.5%) and hexamethylenetetramine (HMT, 99.5%) solutions as starting materials, both obtained from Merck Company. Ce(NO₃)₃·6H₂O and HMT were dissolved in 25 ml distilled water with the various concentrations ranged from 0.005 M to 1 M and 0.05 M to 3.5 M respectively. The reactions were carried out at various temperatures (25°C, 40°C, 65°C, and 90°C) with stirring rate of 3 rpm. Initially, a slightly yellow suspension was precipitated. Subsequently, the precipitates turned into purple, and finally became yellow. To suppress the reaction, after reaching the targeted reaction time, the samples were cooled in the refrigerator at 17°C with an average cooling rate of 0.5 deg./min

The systems were centrifuged at the rate of 10000 rpm for 10 min, the supernatant solutions discarded and precipitates were washed with distilled water and ethanol for four and two times, respectively. The precipitate was left in air for 24 hr and finally dried at 50°C overnight. Table 4.1 and Fig. 4.1 show details of reactions conditions and experimental procedures. The experimental variables of HMT and cerium nitrate concentration were defined considering the optimum experimental conditions reported by other authors [57-59]. To extend the other studies and to investigate wider ranges of experimental variables, the series of experiments based on the trial and error method were also carried out, and it was observed that, for reaction times shorter than 5 hr, the reactions were not completed, and ceria precipitated was not

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enough for the experimental analysis, and beyond the reaction time of 96 hr or sometimes 288 hr, the precipitation reactions reached the steady state, so it was not necessary to continue the experiments for the longer reaction times. It was also observed that, below the reaction temperature of 25°C, the dehydration of ceria precipitate was not completed, and beyond 90°C (near the boiling point of water) the water-based solution started boiling, so the reaction temperatures ranged from 25°C to 90°C were adopted here to investigate thermal activity of ceria precipitation. Considering the effects of temperature on particle size and yield percentage of samples D (section 5.4), the moderate reaction temperature of 40°C was applied for samples A, B, C, H series, and Ce series.

Table 4.1: Experimental conditions.

Sample Name	Ce(NO ₃) ₃ .6H ₂ O Concentration (M)	HMT Concentration(M)	Reaction Temp. C°	Reaction Time(hr)
A	0.3	1.5	40	5, 10, 24, 48, 96
B	0.3	1	40	5, 24, 48, 96, 288
C	0.1	1.5	40	5, 24, 48, 96, 288
D	0.1	1	25, 40, 65, 90	5, 24, 48, 96, 288
H series	0.1	0.05, 0.1, 0.5, 1, 1.5, 2.5, 3.5	40	24
Ce series	0.005, 0.01, 0.1, 0.3, 0.5, 1	1	40	24

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Fig. 4.1. Flow diagram of experimental procedures.

4.1.2. Measurements and Characterization of Synthesized Nano Powder

4.1.2.1. Yield Percentage and Ceria Concentration

Nanocrystalline CeO₂ was produced without heat treatment using HMT as a precipitant and Ce³⁺ as a reactant salt. The whole processing may undergo three-stage chemical reactions [120]:

- 1) The oxidation of Ce³⁺ to Ce⁴⁺ in solution takes place during precipitation. This is due to alkaline solutions favoring the transfer of Ce³⁺ (Lewis acid) to Ce⁴⁺ (Lewis base).
- 2) Ce⁴⁺ ions undergo strong hydration because of their lower basicity, small size and higher charge. The hydrated Ce⁴⁺ ions can form complex with H₂O or OH⁻ ions in the form of [Ce(H₂O)_x(OH)_y]^{(4-y)+}, where x+y is the coordination number of Ce⁴⁺. Further polymerization of this hydroxide is likely, and both can serve as precursors for the final oxide.
- 3) In solution, polar molecules, such as H₂O, take protons away from the hydroxide complexes as follows:

Thus nanocrystalline CeO₂ can be formed at the low reaction temperature in the solution.

Nanoceria concentrations were obtained by dividing weight of produced CeO₂ with the volume of the solution (50 ml). The yield data were calculated by dividing amount of cerium produced with amount of cerium used as reactant material,

$$\text{Yield Percentage} = \left\{ \frac{\text{Weight of cerium in the produced ceria}}{\text{Weight of cerium in the reactant cerium nitrate}} \right\} \times 100 \quad \text{Eq (4.1)}$$

4.1.2.2. Morphology (Transmission Electron Microscopy (TEM))

The morphology of prepared CeO₂ nanoparticles was observed with a transmission electron microscope (TEM), JEM-2010 from JEOL Company. An appropriate amount of CeO₂ suspension directly taken from the reaction solution was observed under the TEM.

4.1.2.3. Particle Size Measurement and Phase Identification (X-ray Diffraction (XRD))

The particle* size of dried powder was studied with X-ray diffractometer (XRD, PER 1820 model, from PHILIPS) using CuKα₁ radiation with the scanning rate of 0.01 deg/s. The particle size of samples, d_{XRD} , was measured from XRD patterns by applying full-width half-maximum (FWHM) of characteristics peak (111) to Debye Scherer equation [120] given by

$$d_{XRD} = \frac{0.9\lambda}{FWHM \cos \theta} \quad \text{Eq (4.2)}$$

where λ is the X-ray (CuKα₁) wavelength (1.5406 Å in this study), and θ is the diffraction angle for the (111) plane.

4.1.2.4. Agglomeration Size Measurement (Brookhaven Particle Analyzer (PA))

The agglomeration size and distribution was determined by Brookhaven particle analyzer (PA), using a dynamic light scattering (DLS) spectroscopy. In DLS, a laser beam is launched through a sample cell where light is scattered by the molecules [117]. Light scattered at a particular detection angle to the incident beam is collected

* Zhang et al [59] confirmed that, fine ceria powder produced via HMT- Ce(NO₃)₃.6H₂O system has a single crystal particles. Therefore, the crystallite size measured from Eq. 4.2 would be equal to the particle size of synthesized ceria powder.

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via a receiving lens or optic and sent to an avalanche photo diode (APD) or photo multiplier tube where photons are converted to electrical pulses. Molecules or particles undergoing Brownian motion cause intensity fluctuations in the scattered light intensity. This fluctuation in scattered light intensity has a time scale that is related to the speed of the movement of the molecules, and hence, to their hydrodynamic size. The collection of photons into time windows or channels and the subsequent autocorrelation of this data yield the translational diffusion coefficient (D_T). Once D_T has been determined, the hydrodynamic radius (R_H) can be calculated using the Stokes-Einstein Equation

$$R_H = \frac{k_b T}{6\pi\eta D_T} \quad \text{Eq (4.3)}$$

where k_b is the Boltzmann constant (the physical constant relating temperature to energy), T is the absolute temperature in Kelvin, and η is the solvent viscosity. Hence, dynamic light scattering is a fast, non-invasive way to determine the size and distribution of particles and molecules in solutions or dispersions.

To measure the agglomeration size, a diluted suspension (1/150 v/v) of CeO₂ was prepared in ethanol solvent, and then put in ultrasonic bath for 5 minutes to reduce the soft agglomeration of particles. Experiment was carried out with 3 runs (5 min duration) for each sample.

4.2. Sintering and Mechanical Properties

4.2.1. Sample Preparation

Micro size ceria powder (CeO₂, 99.9%, from SIGMA-ALDRICH) with an average particle size of 0.38 μm was used as the raw material in the present study. To make the yttria-doped ceria powder, the desired amounts (0.25, 0.5, 1.5, and 8 mol%) of yttria powder (Y₂O₃, 99.9%, from SIGMA-ALDRICH) with an average particle size of 0.35 μm , and ceria powder were dispersed in ethanol, stirred in the ultrasonic bath for 2 hr, and finally dried in the oven at 50°C. Deagglomeration of powder was done by grinding the dried precipitates in the pistol and mortar for approximately 30 min.

Cylindrical pellets of 10 mm diameter and 3.5 mm thickness were prepared by cold uniaxial pressing at the pressure of 255 MPa. After compaction, the green density of pellets was in the order of 57% of the theoretical density. To investigate the sinterability of undoped ceria samples (PC), the green bodies were heated up with a rate of 5 deg/min and isothermally sintered at the various temperatures (T_s) of 1250°C, 1350°C, 1450°C, and 1550°C, and held for the different sintering times (t_s) from 0 to 14 hr. These sintering parameters (T_s and t_s) were defined by referring to the sintering results reported elsewhere [64-68], and the wider sintering time and sintering temperature ranges adopted in this work are due to investigate the sintering and grain growth mechanisms of ceria powder. In order to prohibit further densification of samples, once reaching the desired temperature and time, the power was turned off immediately, and the samples were cooled of in the furnace. Y₂O₃-doped CeO₂ (YC, named for example 0.25YC) green bodies were heated up with a rate of 5 deg/min, and sintered at the various temperatures of 1550°C and 1700°C without applying any sintering time. The higher sintering temperature of 1700°C adopted for Y₂O₃-doped

samples are due to speed up the densification process while yttria doping will be restricting the grain growth.

4.2.2. Characterization of Raw and Sintered CeO₂ Powder

4.2.2.1. Phase Identification

The crystallite structure of powder and sintered bodies was studied with X-ray diffractometer (XRD, PER 1820 model, PHILIP) with CuK_α radiation and the scanning rate of 0.01 deg/s.

4.2.2.2. Topography, Morphology and Particle Size Measurement

The particle sizes of ceria and yttria micro powders and the microstructures of sintered samples were investigated using the scanning electron microscopy (SEM, JSM-5600LV). The average particle sizes of raw powders were determined by measuring sizes of at least 200 particles. The average post-sintering grain size was determined by SEM micrograph of surface using the linear intercept technique. The average surface roughness (R_a) of samples was measured using Dimension TM 3000 atomic force microscopy (AFM). The scanning area was 5×5 μm.

4.2.2.3. Density Measurement

The green densities were calculated by measuring the weight and dimensions of cylindrical compacts. The density of the sintered samples (average of 5 runs) was determined by the Archimedes method using distilled water as displacement liquid. To measure the relative density, theoretical densities of 7.132 and 5.013 g/cm³ were used for ceria and yttria, respectively [87]. In the case of yttria-doped samples, theoretical densities were calculated according to the rule of mixtures [129].

4.2.2.4. Nano Indentation Properties

The samples were mechanically polished down to 1 μm diamond paste prior to indentation test. The nano indentation was carried out using XP nano indenter with a three-sided pyramidal Berkovich diamond indenter. The samples were loaded to 2 and 50 mN, held for 2 sec then unloaded. The elastic modulus (E) and nano hardness (H_n) (average of at least 20 readings) of samples, at the room temperature were measured from the load-displacement nano indentation data (Fig. 4.2) using the widely accepted Oliver and Pharr method [118].

Fig. 4.2. Typical indentation load data defining key experimental quantities [118].

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The Oliver-Pharr data analysis procedure begins by fitting the unloading curve to the power-law relation

$$P = B(h - h_f)^m \quad \text{Eq (4.4)}$$

where P is the indentation load, h is the displacement, B and M are empirically determine fitting parameters, and h_f is the final displacement after complete unloading. The unloading Stiffness, S , is then established by differentiating Eq. 4.5 at the maximum depth of penetration, $h = h_{\max}$, i.e.

$$S = \frac{dP}{dh}(h = h_{\max}) = mB(h_{\max} - h_f)^{m-1} \quad \text{Eq (4.5)}$$

The correct depth is also estimated from the load-displacement data using:

$$h_c = h_{\max} - \varepsilon \frac{P_{\max}}{S} \quad \text{Eq (4.6)}$$

where $P_{\max}$ is the peak indentation load, and ε is a constant which depends on the indenter geometry. Empirical studies have shown $\varepsilon = 0.75$ for a Berkovich indenter.

Once the contact area is determined from the load-displacement data, the hardness, H , and effective elastic modulus, E_{eff} , follow from:

$$H = \frac{P_{\max}}{A} \quad \text{Eq (4.7)}$$

and

$$E_{\text{eff}} = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \quad \text{Eq (4.8)}$$

where β is a constant which depends on the geometry of the indenter ($\beta = 1.034$ for the Berkovich). The effective modulus, which accounts for the specimen and the indenter, is given by

$$\frac{1}{E_{\text{eff}}} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad \text{Eq (4.9)}$$

where E and ν are the Young's modulus and Poisson's ratio for the specimen, and E_i and ν_i are the same quantities for the indenter.

4.2.2.5. Micro Indentation Testing (Vickers Hardness and Fracture Toughness Testing)

The micro indentation was performed on the selected samples sintered at 1550°C and Ytria-Doped Samples. Sintered specimens were polished with diamond paste before the indentation testing. All the specimens were indented with Vickers indenter FM-300e, with the indentation loads of 0.25 N (Hardness) and 20 N (fracture toughness), and with the indentation time of 5 sec. The average Vickers indentation diagonal half-length (a), and crack length (C) emanating from the indentation corner in each case was measured from at least 10 indentations at indentation loads (P) of 0.25 and 20 N, respectively. The corresponding Vickers hardness (H_V) and fracture toughness (K_{IC}) of the material were calculated using Eq. 4.10 and 4.11 [113],

$$H_V = 0.4636 \frac{P}{a^2} \quad \text{Eq (4.10)}$$

$$K_{IC} = 0.016 \left(\frac{E}{H} \right)^{0.5} \frac{P}{C^{1.5}} \quad \text{Eq (4.11)}$$

Chapter 5: Synthesis and Growth Kinetics of Nano CeO₂ Powder

5.1. Introduction

Particle size and morphology of synthesized nano ceria powder have a significant effect on efficiency of powder in its industrial applications. Smaller particle sizes result in better reactivity in the catalytic applications, and better dispersity and auto catalytic behavior of powder in the biomedical applications. However, yield percentage is also an important processing factor that should be considered for economical concerns. The following chapter investigates effects of reaction temperature, precipitant (HMT) concentration, and reactant salt (CeNO₃.6H₂O) concentration on the particle size, poly dispersity index and yield percentage of synthesized nano ceria powder.

An understanding of the factors that affect particle growth kinetics and microstructure development in nanocrystals is fundamental to control nano particle properties. Existing kinetic models for coarsening are described by Ostwald ripening or oriented attachment mechanism. The kinetics model of particle growth strongly depends on the structure of the material, the properties of the solution, and the nature of the interface between the crystals and the surrounding solution. In order to find an approach for better control of particle size, the following chapter also studies the kinetics of nano ceria processing, and reveals effects of various processing parameters, such as reactants concentration and reaction temperature on the particle growth mechanism and kinetics constants of reactions.

5.2. Morphology of Synthesized Nano CeO_2 Powder

Fig. 5.1 shows TEM image of CeO_2 nano particles produced at 40°C . The electron diffraction pattern recorded from the area can be indexed according to the CaF_2 -type structure.

Fig. 5.1. TEM images of samples D, 40°C (a) 5 hr showing irregular shape, and (b) 48 hr showing faceted particles. Inset: Electron diffraction pattern of synthesized ceria.

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Particles produced in sample D, 40°C, 5 hr (10.5 nm) revealed irregular shapes, whereas particles produced in sample D, 40°C, 48 hr (34.1 nm) were mostly faceted. Fig. 5.2 shows octahedral particles produced in sample C at the reaction temperature of 40°C for the various reaction time of 5 (17.8 nm) and 24 hr (25.6 nm). In fact, with increase of particle size the morphology changed to cubic shapes which are, according to Zhang studies [59], enclosed with eight {111} surfaces.

Fig. 5.2. TEM images of samples C, 40°C (a) 5 hr, and (b) 48 hr showing faceted particles.

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In general, TEM observations have revealed three kinds of morphology for the synthesized nano ceria particles [2, 59]: a) the octahedral shapes, b) the {200} truncated-octahedral shapes, and c) the irregular shapes (Fig. 5.3).

Fig. 5.3. A lattice images of nano ceria particles along its [110] direction showing two and three dimensional projections of tetragonal shape (a and b), two {200} truncated-octahedral shape(c and d), and irregular shape (e) [59].

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As a summary of the TEM observations, the octahedral and {200} truncated-octahedral are the most popular shapes. To understand this result, unit cell structure of CeO₂ should be considered. The unit cell of CeO₂ is made of a face centered cubic (fcc) structured Ce lattice and a cubic oxygen cage located inside the fcc cation lattice. Naturally, this structural configuration may have some similarity to the fcc lattice. From the structure model for the (100), (110), and (111) planes, the surface density of atoms in the corresponding planes follows $n(111) > n(200) > n(110)$. For a fcc structured metal, the surface energy for the three lowest index planes follows: $\gamma\{111\} < \gamma\{200\} < \gamma\{110\}$. The above experimental data suggest that this rule may also hold for CeO₂.

Fig. 5.4 shows TEM image of samples A and B, at 40°C, for 5 hr. Particles produced here were nearly spherical. According to Dirksen study [116], degree of saturation has a significant effect on the morphology of particles produced via homogeneous precipitation system. Higher degree of cerium nitrate and HMT concentration of samples A and B synthesized at 40°C for 5 hr resulted in higher ceria concentration or saturation (Fig. 5.13). Consequently, the nearly spherical morphology obtained here can be attributed to the increase of saturation which would result in increment of nucleation rate and the randomly attachment of atoms to the primary particles [116].

Fig. 5.4. TEM images of samples (a) A, 40°C, 5 hr, and (b) B, 40°C, 5 hr showing nearly spherical particles.

5.3. Effect of Reactants Concentration on the Particle Size and Yield Percentage of Synthesized Nano CeO₂ Powder

5.3.1. Effect of HMT Concentration

Hirano et al [53] showed that, the particle size of synthesized ceria continuously decreased with the increase of urea concentration due to the increase of saturation and nucleation in the basic solution (Fig. 5.5). However, the results obtained here revealed more complicated effects of precipitant concentration.

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Fig. 5.5. Effect of urea concentration on the crystallite size of CeO₂ [53].

Fig. 5.6. Particle size (length, width) of process A with the addition of different urea concentrations against the aging period [119].

Lin et al [119] investigated effect of urea concentration on the particle size of synthesized indium hydrate. They revealed that the particle size increased with the increase of urea addition as the concentration of urea was ≤ 1.0 mol/l, and reached the largest value of about 1300 nm in length, and 300 nm in width, but decreased when more urea was added (Fig. 5.6). A similar effect of precipitant concentration on the particle size of synthesized powder was obtained in the present work. Fig. 5.7 shows effect of HMT concentration on the particle size of synthesized ceria. It was observed that, particle size of ceria firstly increased with the increase of HMT concentration, and then decreased. This can be explained by considering the degree of ceria super saturation or ceria concentration which is displayed in Fig. 5.8. Considering the data in Figs. 5.7 and 5.8, the direct relationship between the particle size and ceria saturation is concluded. In fact, higher amounts of saturation resulted in the bigger particle size by increasing the nucleation rate (Eq. 3.12) and activating oriented attachment (OA) mechanism of particle growth [116] due to the reduction of inter-nuclei distances (this will be discussed in detail in section 5.5).

$$\log\left(\frac{j}{j_{\max}}\right) = -A[\log(S)]^{-2} \quad \text{Eq (3.12)}$$

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Fig. 5.7. Effect of HMT concentration on the particle size of produced ceria (H series synthesized at 40°C). For these samples the cerium nitrate concentration is kept constant at 0.1 mol/l. R is the HMT-to-cerium nitrate molar ratio.

Fig. 5.8. Effect of HMT concentration on the degree of ceria concentration for H series synthesized at 40°C.

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Fig. 5.8 indicates that, ceria saturation itself depended on not only HMT concentration but also HMT to cerium nitrate molar ratio (R). Increase of R up to a critical point (this may be a stoichiometric ratio that is predicted according to the balancing of relevant chemical reactions) resulted in higher ceria concentrations due to providing enough material (HMT) for completion of reactions, but beyond this critical point, increase of R resulted in the increase of H₂O and OH⁻ ions and formation of complicated Ce-complexes (as it was obvious from the nearly pinkish yellow color of precipitates [120]), which cannot dehydrate easily to form the ceria precipitation [46]. In this case, lower amounts of ceria concentration caused the particle sizes to decrease.

The fluctuation at the beginning of diagram can be attributed to experimental errors or effect of concentration increment, which decreased nuclei (Eq. 3.4) and particle size as a result.

$$r^* = \frac{2\beta_a \gamma v}{3\beta_v k_B T \ln(s)} \quad (3.4)$$

Li [120] has reported R value of 3 for Ce³⁺-NH₄⁺ system. In this work a critical value of 15 was obtained for Ce⁴⁺-HMT system, however further work is required to define the exact critical R value.

Fig. 5.9 shows effect of HMT concentration on the yield percentage of reactions. As it is expected, plot of yield data versus HMT concentration looks similar to that of ceria concentration (Fig. 5.8). The maximum point observed in Fig. 5.9 can be explained by considering effect of R value on the degree of saturation. Small amounts of yield percentage (less than 50%) obtained for H-series samples can be attributed to a low reaction temperature or a small amount of cerium nitrate concentration (0.1 mol/l) used here.

5.3.2. Effect of Cerium Nitrate Concentration

Figs. 5.10 and 5.11 show effect of cerium nitrate concentration on the particle size and ceria concentration of Ce series, respectively. The HMT concentration was constant here, so increase of cerium nitrate concentration resulted in decrease of R value (favorite for increase of saturation), and also it cumulatively provided enough cerium nitrate for completion of reactions. The particle size therefore increased consistently with the increase of cerium nitrate concentration due to the increase of ceria saturation.

Fig. 5.9. Effect of HMT concentration on the yield percentage of produced ceria (H series synthesized at 40°C).

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Fig. 5.10. Effect of cerium nitrate concentration on the particle size of produced ceria (Ce series synthesized at 40°C). For these samples the HMT concentration is kept constant at 1 mol/l.

Fig. 5.11. Effect of cerium nitrate concentration on the degree of ceria concentration for Ce series synthesized at 40°C.

5.3.3. Effect of Both HMT and Cerium Nitrate Concentration

Fig. 5.12 and Fig. 5.13 show the effects of reactants concentration on the particle size and saturation of ceria produced from samples A, B, and C at 40°C. Particle size increased with the reaction time for all the three different concentrations of reactants. Sample A with the highest concentration of both HMT and cerium nitrate produced the biggest particle sizes, but its particle size converged to that of sample B with the same cerium nitrate concentration but higher HMT concentration after a reaction time of 48 hr. This may be attributed to the limiting effect of HMT (sample A has the higher amount of R value) which prohibits further precipitation and particle growth of sample A after a reaction time of 48 hr. As it is also obvious from Fig. 5.13, after a reaction time of 48 hr ceria concentration in sample A became lesser than sample B. Comparing the plot of sample A with that of sample C, a higher concentration of cerium nitrate in sample A resulted in the larger particle sizes compared to the sample C at the same reaction time.

In general, less agglomerated powders with the better properties were obtained for the R values around 5. Kang et al [121] also have shown the significant effect of R (oleic acid to copper sulfide ratio) on the friction reducing and antiwear properties of CuS nanoparticles synthesized with chemical method.

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Fig. 5.12. Effect of reactants concentration on the particle size of ceria powder prepared from samples 0.3 mol/l cerium nitrate-1.5 mol/l HMT (A), 0.3 mol/l cerium nitrate-1 mol/l HMT (B), and 0.1 mol/l cerium nitrate-1.5 mol/l HMT (C) at a reaction temperature of 40°C.

Fig. 5.13. Effect of reactants concentration on the degree of ceria concentration for samples 0.3 mol/l cerium nitrate-1.5 mol/l HMT (A), 0.3 mol/l cerium nitrate-1 mol/l HMT (B), and 0.1 mol/l cerium nitrate-1.5 mol/l HMT (C) synthesized at 40°C.

Effects of reactants concentration on the yield percentage of samples A, B and D synthesized at 40°C is illustrated in Fig. 5.14. In spite of having lowest degree of reactants concentration, samples D revealed maximum degree of yield percentage due to their smallest degree of cerium nitrate concentration (Refer to Eq 6.1) compared to samples A and B. Therefore, it is concluded that the yield data are more useful for the economical consideration rather than estimating saturation or predicting particle size and growth mechanism of samples. In the optimum condition, acceptable yield of 76.6% was obtained for sample A, synthesized at 40°C for 96 hr (particle size = 34.1 nm).

5.4. Effect of Reaction Temperature on the Particle size, Polydispersity Index and Yield Percentage of CeO₂ Powder

Fig. 5.15 shows the XRD patterns of samples D, synthesized at 65°C, for the various reaction times of 5, 24, 48, and 96 hr. The characteristics peaks occurred at approximately $2\theta = 28.5, 33.1, 47.5, 56.3$ and 59.0 were confirmed as the cubic fluorite structure CeO₂. As it is obvious from the XRD patterns, the width of characteristic picks (111) decreased with increase of reaction time. Such a trend implies an increase of CeO₂ particle size with the reaction time.

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Fig. 5.14. Effect of reactants concentration on the yield percentage of produced ceria from samples 0.3 mol/l cerium nitrate-1.5 mol/l HMT (A), 0.3 mol/l cerium nitrate-1 mol/l HMT (B), and 0.1 mol/l cerium nitrate-1 mol/l HMT (D) at a reaction temperature of 40°C.

Fig. 5.15. XRD patterns of samples D synthesized at 65°C for the various reaction times of 5, 24, 48 and 96 hr.

5.4.1. Effect of Reaction Temperature on the Particle Size

Effect of reaction temperature on the particle size of CeO₂ produced from samples D is summarized in Fig. 5.16. In general, the particle size increased with the reaction temperature and reaction time up to 96 hr. This is because; increase of reaction temperature promoted ceria concentration (Fig. 5.17) due to the enhanced production of CeO₂ from the hydrated $\text{Ce}(\text{OH})_y(\text{H}_2\text{O})_x^{(4-y)+}$ or $\text{CeO}_2 \cdot n(\text{H}_2\text{O})^{(4-y)+}$ at the elevated temperatures [53]. Degree of ceria concentration for samples D, 40°C and D, 65°C was approximately same, but bigger particle sizes were obtained at the reaction temperature of 65°C. The effect of reaction temperature here can be explained by considering the enhancement of atomic diffusion which speeds up particle growth at the higher reaction temperatures. However, particle size increased with the reaction temperature for all the four different reaction temperatures. Hence, it can be concluded that the growth rate, which is relating to enhancement of diffusion or oriented attachment mechanism (increase of particle size) was predominant over the nucleation rate (increase of nucleation rate and decrease of critical nucleation size (Eq. 3.4) and particle size) with increase of reaction temperature.

As it is obvious from Fig. 5.16, the particle growth rate of samples synthesized at 25°C, 40°C, and 65°C decreased significantly beyond the reaction time of 96 hr. This is because; the steady state of reaction was reached due to the entire reactant materials being consumed or the maximum amount of yield being reached beyond 96 hr. The unusual maximum observed at the reaction temperature of 90°C can be explained by the larger polydispersity of particle size for the longer reaction time, which would cause inaccuracy in measurement of average particle size.

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It is noteworthy that, in spite of producing the smallest particle size at reaction temperature of 25°C, lack of diffusion at this temperature resulted in the production of dark yellow and coarser (bigger agglomeration size) powders. This is probably because of incomplete dehydration reactions at the lower reaction temperatures. In general, coarser powders were obtained with decrease of reaction temperature and particle size.

Fig. 5.16. Effect of reaction temperature on the particle size of ceria prepared from samples D (0.1 mol/l cerium nitrate-1 mol/l HMT).

Fig. 5.17. Plots of ceria concentration versus reaction time for samples D synthesized at the various temperatures.

5.4.2. Effect of Reaction Temperature on the Homogeneity of Powder

Effect of reaction temperature on the homogeneity of particles is shown in Fig. 5.18. The PA diagram shows the polydispersity of particles produced from sample D at 40°C. Polydispersity index of 0.12 was obtained for reaction temperature of 40°C. A more homogeneous structure with polydispersity index of 0.09 was obtained with increase of reaction temperature up to 65°C. This can be explained by considering a single burst of nucleus and enhancement of atomic diffusion with increase of reaction temperature. However agglomeration of particles was clear in both cases. Average agglomeration sizes of 153.3 nm and 199.3 nm were obtained for particles synthesized at 40°C and 65°C, respectively.

Fig.5.18. PA of samples D for 5 hr with a reaction temperature of (a) 40°C, and (b) 65°C.

5.4.3. Effect of Reaction Temperature on the Yield Percentage

Effect of reaction temperature on the yield percentage of reactions is shown in Fig. 5.19. As the higher temperatures facilitate production of CeO₂ from the hydrated Ce(OH)_y(H₂O)_x^{(4-y)+} or CeO₂.n(H₂O)^{(4-y)+} [53], yield percentage increased with the increase of reaction temperature. A maximum yield of 81% was obtained for sample D with a reaction temperature of 90° C for 96 hr, however the powder produced here was not very fine (particle size = 66.5 nm). In the optimum condition, an acceptable yield of 75% and a particle size of 41.0 nm were obtained for sample D synthesized at 40°C for 96 hr. The unusual maximum of curve at 40°C may be due to experimental error.

Fig. 5.19. Effect of reaction temperature on the yield percentage of samples D synthesized at the various temperatures.

5.5. Kinetics of Particle Growth

5.5.1. Ostwald Ripening Mechanism

A saturated solution will initially contain a large number of particles or crystals. Due to the thermodynamical stability of system, smaller particles tend to precipitate onto the larger particles. Smaller particles therefore act as “nutrients” for the bigger particles and the average particle size will increase. The rate of this process called Ostwald ripening decreases as the particles grow and the particle size distribution becomes narrower [122].

This spontaneous process occurs because larger particles are more energetically favored than smaller particles (Fig. 5.20). While the formation of many small particles is kinetically favored, (i.e., they nucleate more easily) large particles are thermodynamically favored. This is because; small particles have a larger surface area-to-volume ratio than large particles and are consequently easier to produce.

Fig. 5.20. Particle growth via Ostwald ripening mechanism [123].

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Molecules on the surface are energetically less stable than the ones already well ordered and packed in the interior. Large particles, with their greater volume-to-surface area ratio, therefore represent at a lower-energy state. Hence many small particles will attain a lower-energy state if transformed into large particles and this is what we see in Ostwald ripening.

The rate law can be derived from the Gibbs Thomson equation and Fick's law, but the main result is [124]:

$$D - D_0 = kt^{1/n} \quad \text{Eq (5.1)}$$

where [122],

$$k = \frac{8\gamma D V_m^2 C_\infty}{9RT}, \quad \text{Eq (5.2)}$$

t is time, n is kinetic crystallite-growth exponent, and D_0 is the average particle diameter at $t = 0$, C_∞ is the equilibrium concentration at a flat surface, γ is the interfacial energy, V_m is the molar volume of the solid (mol cm^{-3}), D is the diffusion coefficient, R is the gas constant, and T is the temperature (K). Hence a plot of $\ln$ (particle size) versus $\ln$ (time) should be linear if the particle growth follows Ostwald ripening. In this case, the exponent n ranged from 2 to 4, and it is deduced that growth is controlled by diffusion of atoms, or the dissolution kinetics at the particle matrix interface.

Some studies [122, 124, 125, and 126] have revealed activation of Ostwald ripening mechanism for the particle growth of ZnS and ZnO nano powder. In the present work it is shown that the particle growth of nano ceria can be also fitted by Ostwald ripening mechanism consistent with growth controlled by the diffusion of ions in the solution.

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Particle growth kinetics of samples B and C has been studied at 40° C. For both samples, the plots of $\ln$ (particle size) versus $\ln$ (time) were satisfactorily fitted by straight line (Fig. 5.21). The kinetic crystallite-growth exponents n , calculated from the slopes were 2.48 and 4.88 for samples B and C, respectively. These values indicate a diffusion controlled particle growth (Ostwald ripening) mechanism for the CeO₂ powder obtained for the two samples.

Fig. 5.22 shows $\ln$ (particle size) versus $\ln$ (time) fitted plots for samples D for the different reaction temperatures (since Eq. 5.1 is not applicable to the steady state of particle growth, the data beyond 96 hr were eliminated in this plot). The values of n from the slopes were 2.23, 2.05, 1.91, and 2.01 for the reaction temperatures of 25°C, 40°C, 65°C, and 90°C, respectively. These close values suggest a similar crystallite growth mechanism of Ostwald ripening for the CeO₂ samples at the different reaction temperatures. However, the fitting results for the samples synthesized at the lower reaction temperatures of 25 and 40°C show larger deviations from the straight line.

It is noteworthy that, the data shown in Fig. 5.21 and 5.22 were also curve fitted by polynomial curve (power = 2). In all cases, lower standard deviations were obtained for the straight line fitting of data. Audebrand et al [43] have also investigated n values for ceria particles grown in the saturated solution. They have reported n values of 5.1 and 4.6 for the ceric ammonium-ammonia and cerium sulfate-ammonia systems, respectively. Compared to the present work, these differences in n value can be attributed to the different systems which are used to get ceria precipitates.

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Fig. 5.21. Plots ln (particle size) versus ln (time) for samples 0.3 mol/l cerium nitrate-1 mol/l HMT (B) and 0.1 mol/l cerium nitrate-1.5 mol/l HMT (C) prepared at 40°C.

Fig. 5.22. Plots ln (particle size) versus ln (time) for samples D prepared at the various reaction temperatures.

Table 5.1 summarizes the fitting results for samples B, C, and D at the various reaction temperatures. It seems that the value of the exponent n was more dependent on the reactant concentration than the reaction temperature. As it is expected, k increased continuously with the increase of reaction temperature.

Dependence of k to temperature is defined by the Arrhenius equation [21],

$$\ln k = -\frac{E_a}{RT} + A_0 \quad \text{Eq (5.3)}$$

where E_a is the activation energy, A_0 is the preexponential factor, R is the universal gas constant, and T is the absolute temperature.

From the Arrhenius plot of various kinetic constants (Fig. 5.23) at the various reaction temperatures, the activation energy of Ostwald ripening, $E_a = 9.06 \text{ kJmol}^{-1}$ was obtained for sample D. The activation energies of 221, 153, and 65 kJmol^{-1} have been reported for the nano ceria powder prepared from decomposition of ceric ammonium, cerium sulfate and ammonium ceric nitrate, respectively [43]. These results show that, precursor chemicals have a significant effect on the crystallite growth rate.

5.5.2. Oriented Attachment Mechanism

Fitting of the data for Sample A using Eq. 1.1 yielded an exponent of 10.10. Such a large exponent has no physical meaning. Thus a new kinetic model is required to explain the experimental result. In the oriented attachment (OA) based coarsening, two small nano particles combine to form a larger particle without the dissolution of either particle. Growth via OA is controlled by the probability of contact between nanoparticles in appropriate orientations. The OA based growth of nanocrystals is related to the number of initial particles in a given volume (i.e., the “concentration” of nanoparticles) [124].

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Table 5.1. Fitting parameters for samples A, B and C.

Sample Name	Temp. (C)	n	k (hr ⁻¹)
A	40	10.10	22.96
B	40	2.48	5
C	40	4.88	13.09
D	25	2.23	3.49
	40	2.05	4.33
	65	1.91	4.77
	90	2.01	7.13

Fig. 5.23. Arrhenius plot of the kinetic constant k for sample D.

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Suppose that the initial average particle size and number are, respectively, D_0 and N_0 at $t = 0$. After growth via oriented attachment for a period of time t , the number of initial particles is $N(t)$, and the number and the average particle size of grown particles are $N_2(t)$ and D_2 , respectively.

According to the principle of mass balance [124],

$$\frac{1}{6}\pi\rho D_0^3 N_0 = \frac{1}{6}\pi\rho D_0^3 N(t) + \frac{1}{6}\pi\rho D_2^3 N_2(t) \quad \text{Eq (5.4)}$$

where ρ represents the density of CeO₂.

Assuming OA of 5 particles, minimum standard error for the fitting constants was obtained. Since $V_2 = 5V_0$, $D_2 = \sqrt[3]{5} D_0$, and we have,

$$N_2(t) = (N_0 - N(t))/2 \quad \text{Eq (5.5)}$$

The oriented attachment rate, the number of initial particles reacted in an unit time, can be written as

$$-\frac{dN(t)}{dt} = kN(t)^2 \quad \text{Eq (5.6)}$$

By integrating Eq 5.6, we have

$$\frac{1}{(N(t)/N_0)} = k_1 t + 1 \quad \text{Eq (5.7)}$$

where $k_1 = kN_0$

According to the definition of the volume-weighted average particle size which is consistent with the average particle size determined by XRD using the Scherrer method, the average particle size D in the first stage can be related to D_0 and D_2 by

$$D = \frac{D_0(\sqrt[3]{5}kt + 1)}{(kt + 1)} \quad \text{Eq (5.8)}$$

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Huang et al [124] have shown that ZnS nano particles can grow via OA mechanism. Lee et al [127] also have revealed that OA mechanism occurs in the hydrothermal coarsening of nanocrystalline TiO₂. In continuation of these speculations, it can be shown in this work that, OA is also a dominant mechanism in particle growth of CeO₂ powder produced from sample A synthesized at 40°C.

The particle growth of sample A fits well using Eq. 5.8, with D_0 and k as the least-squares fitting parameters (Fig. 5.24). The values of 21.25 and 0.11 were obtained for D_0 and k , respectively. Among all the samples, sample A had the highest concentration of both cerium nitrate and HMT, so it would be expected to react faster. This resulted in the highest degree of ceria concentration or saturation for the same reaction time (Fig. 5.13 and 5.17).

Fig. 5.24. Fitting result showing particle size versus reaction time for sample A prepared at 40°C.

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Considering Eq. 3.13, increase of ceria concentration would increase the nucleation rate, which would result in activation of OA mechanism due to the reduction in the inter-molecular distances [116],

$$\log\left(\frac{J}{J_{\max}}\right) = -A[\log(S)]^{-2} \quad \text{Eq (3.13)}$$

J: nucleation rate

A: temperature dependent rate constant

S: saturation

Therefore, the OA of primary particles is more probable for sample A because of its highest reactants concentration compared to the others. However, the synthesized nano size particles were very small and had a high tendency to agglomerate in order to reduce surface free energy. So, even at the lower reactants concentration, OA mechanism would accompany Ostwald ripening for further particle growth.

5.6. Conclusions

- i. Increase of both cerium nitrate and HMT concentration resulted in spherical particles' morphology, e.g. a nearly hexagonal or spherical particles were obtained from sample A (0.3 mol/l cerium nitrate-1.5 mol/l HMT) with the highest degree of reactants concentration synthesized at 40°C for 5 hr.
- ii. Increase of particles size led to formation of more faceted particles due to the faster growth of particles along {111} surfaces. A faceted particle of 17.0 nm was obtained from sample D (0.1 mol/l cerium nitrate-1 mol/l HMT) synthesized at 40°C for 48 hr.

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- iii. Various particle sizes of 8.5 to 68.2 nm were produced under various experimental conditions. It was observed that, degree of saturation was the most important factor that affected particle sizes of synthesized nano ceria powder. Degree of saturation itself depended on various experimental parameters, such as reactants concentration, reaction time and reaction temperature.
- iv. In general, the particle sizes increased with increase of reaction time and reaction temperature due to the increase of ceria concentration or saturation.
- v. Increase of HMT concentration initially increased the particle size then decreased it. It was therefore concluded that, not only the reactant concentration but also the HMT to cerium nitrate molar ratio (R) affects saturation and particle size as a result. Increase of cerium nitrate concentration consistently increased the particle size.
- vi. Degree of yield percentage increased with the reaction temperature. In the optimum condition, an acceptable yield of 75% and a particle size of 41 nm were obtained for sample D (0.1 mol/l cerium nitrate-1 mol/l HMT) synthesized at 40°C for 96 hr.
- vii. In general, less agglomerated powders with better properties were obtained for R values around 5.
- viii. It was observed that, with the increase of reactants concentration the grain growth mechanism changed from Ostwald ripening to an oriented attachment mechanism due to the increase of ceria concentration or saturation.

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- ix. By plotting $\ln(k)$ versus $1/T$, small activation energy of 9.06 kJ was obtained for the particle growth of sample D (0.1 mol/l cerium nitrate-1 mol/l HMT) via Ostwald ripening mechanism.

Chapter 6: Sintering Behavior of Undoped and Y₂O₃-doped CeO₂ Powder

6.1. Introduction

Being a refractory material, CeO₂-based materials are difficult to densify even when sintered at higher temperatures, and increase of sintering temperature in order to approach the full density would result in significant grain growth, which would deteriorate mechanical and electrical properties of ceria as a result. According to the literature [70, 71] Y³⁺ exhibits the most effective suppression of grain growth among all the investigated dopants. Y₂O₃-doped CeO₂ is also a good candidate for SOFCs applications [73]. For the cost effectiveness we used CeO₂ commercial powder as the starting materials, and explored the various amounts of Y₂O₃ doping to suppress the grain growth of ceria samples. The first part of following chapter focuses on the sintering behavior and final stage ($\rho \geq 90\%$) sintering mechanism of undoped micro CeO₂ powder, and second part will discuss the sintering behavior and post-sintering grain size of Y₂O₃-doped CeO₂.

6.2. Sintering and Post-sintering Grain Size of Undoped CeO₂ Powder

Fig. 6.1 shows the densification result of micro ceria powder sintered at the various temperatures of 1250°C, 1350°C, 1450°C, and 1550°C. In general, the relative density increased with the sintering temperature due to the enhancement of atomic diffusion at the higher temperatures. For the same sintering time of 2 hr, relative densities of

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76.00% and 98.60% were obtained for the samples sintered at 1250°C and 1550°C, respectively. The effect of sintering time to increase the relative density of samples was much more significant at the lower sintering temperatures of 1250°C and 1350°C. In fact, beyond the relative density of 97%, at any sintering temperature, sintering time didn't have any significant effect to enhance the sinterability of samples. The maximum relative density of 98.86% (grain size = 29.7 μm) was obtained for PC sample sintered at 1550 for 4 hr.

Fig. 6.2 illustrates the post-sintering grain size of undoped ceria powder at the various sintering temperatures. The grain size of samples significantly increased at the higher sintering temperatures of 1450°C and 1550°C (due to the enhancement of atomic diffusion with temperature), whereas it remained almost constant at 1250°C and 1350°C. As the sintering time increased, grain size increased as well. However, beyond a sintering time of 10 hr, grain sizes of samples sintered at 1450°C and 1550°C decreased sharply. This can be attributed to the large polydispersity index of grains for a long sintering duration (14 hr) which causes inaccuracy in the average grain size measured by applying linear interception method.

Considering both Fig. 6.1 and 6.2, it can be deduced that, a higher sintering temperature promotes the densification process of ceria micro powder, but it undesirably results in significant grain growth, which would deteriorate mechanical and electrical properties of CeO₂ samples. However, samples sintered at 1350°C and 1450°C relatively had both advantageous of higher relative density and smaller grain size. In the optimum condition, the relative densities of 97.60% and 98.23%, and grain sizes of 1.1 and 14.2 μm were obtained for the samples sintered at 1350°C and 1450°C for sintering times of 8 and 10 hr, respectively.

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Fig.6.1. Relative density results of CeO₂ samples sintered at the sintering temperatures of 1250°C, 1350°C, 1450°C, and 1550°C for the various sintering times.

Fig.6.2. Post-sintering grain size of CeO₂ samples sintered at the sintering temperatures of 1250°C, 1350°C, 1450°C, and 1550°C for the various sintering times.

6.3. Grain Growth and Final Stage Sintering

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6.3.1. Grain Growth Mechanism

Grain growth kinetics can be described via the following equation [71],

$$\frac{\delta D}{\delta t} = \frac{M\gamma}{D} \quad \text{Eq (6.1)}$$

where D is the average grain size at the time t , M is the mobility of grain boundary, and γ is the grain boundary energy. If both M , and γ are independent of time, then Eq. 6.1 leads to the parabolic law for grain growth,

$$D^2 - D_0^2 = 2M\gamma(t - t_0) = k(t - t_0) \quad \text{Eq (6.2)}$$

$$k = k_0 \exp\left(\frac{-Q}{RT}\right) \quad \text{Eq (6.3)}$$

where k is the rate constant, K_0 is the preexponential constant, Q is the activation energy of grain growth, R is the universal gas constant, and T is the temperature. The growth exponent of 2 implies that, grain growth is controlled by the boundary mobility where the atomic diffusion occurs across the grain boundaries [71, 128].

In reality, it is also common to find nonparabolic growth with a growth exponent varying from 2 to 4. This can be interoperated as due simply to a decreasing mobility. Surface diffusion, grain boundary or bulk diffusion of atoms may be dominant mechanisms in this case, and the grain growth kinetics can be described by the following equation [129],

$$D^n - D_0^n = k(t - t_0) \quad \text{Eq (6.4)}$$

where $n = 3$ to 4.

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To find out the dominant mechanism of grain growth, we plotted $D^n - D_0^n$ ($n = 2, 3,$ and 4) against reciprocal time ($t - t_0$) using the grain size data in Fig. 6.2. As it is obvious from the fitting results of Fig.6.3a, b, and c, the data relatively fitted well with the straight line for all the three different values of n (at the specific sintering temperature, the R-squared values (Table 6.1) are approximately the same for all the n values of 2, 3, and 4). It was therefore concluded that fitting results do not uniquely

Fig. 6.3. Grain growth kinetics of CeO₂ samples at the sintering temperatures of 1250, 1350, 1450, and 1550°C for the different n values of 2 (a), 3(b), and 4(c).

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Table 6.1. R-squared value for the straight line fitted results of CeO₂ grain growth at the various sintering temperatures.

Sintering Temperature (k)	R-Squared Value		
	n = 2	n = 3	n = 4
1250	0.8235	0.8416	0.7380
1350	0.9445	0.9619	0.9601
1450	0.936	0.9243	0.9019
1550	0.9607	0.9916	0.9718

determine n value nor the grain growth mechanism by themselves. However, for all the various sintering temperatures, except 1450°C, R-squared had a maximum value for the growth exponent of 3. Samples sintered at 1250°C showed a larger deviation (low R-squared value) from the straight line for all the values of n. This may imply that, none of the above mentioned mechanisms are applicable at the sintering temperature of 1250°C due to the very slow grain growth of samples at the lower temperatures.

Zhang et al [129] reported the n value of 3 for undoped micro ceria powder assuming D_0^n to be negligible relative to D^n . However, this estimation cannot be very accurate especially at the lower sintering temperatures where the grains grow very slowly. Chen and Chen [71] reported n value of 2 for the grain growth of nano ceria powder, and, same as the present results, some researches [130, 131] found their result can be fitted well using both n = 2 and 3. However, there are many factors, including

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grain size, interfacial energy, interface anisotropy, and grain interlocking which control the sintering process, and all these results, in fact, just reflect the complexity of sintering mechanism.

The activation energy (Q) can be obtained from the slope of an Arrhenius plot of $\ln(k)$ versus $1/T$ based on Eq. 6.3. Fig. 6.4 shows the straight line fitted data for the micro ceria powder considering various amounts of grain growth exponent, n . The activation energies of 673.03, 976.61, and 1287.19 kJ/mol were obtained for the n values of 2, 3, and 4, respectively. The activation energies obtained here are comparable to the reported activation energy of 731 kJ/mol for the micro ceria powder [132]. Chen and Chen [70] reported smaller activation energy of 581 kJ/mol for grain growth of nano ceria powder. However, it seems to be logical for the nano powder to have the smaller value of Q due to its larger surface area, which speeds up atomic diffusion and facilitates the grain growth of samples.

Fig. 6.4. Arrhenius plot of CeO₂ samples for $n = 2, 3$, and 4.

6.3.2. Sintering Mechanism

The densification data in the final stage of sintering ($\rho > 90\%$) were analyzed assuming a conventional sintering mechanism governed by either lattice diffusion or grain boundary diffusion. The rate equation for these mechanisms is generally written in the form of modified Herring's law, Eq. 6.5,

$$\frac{d\rho}{dt} = \frac{f(\rho)}{kTD^m} C_0 \exp\left(-\frac{Q}{kT}\right) \quad \text{Eq (6.5)}$$

where ρ is density, t is time, T is temperature, D is grain size, m is 3 for lattice diffusion control and 4 for grain boundary diffusion control, Q is activation energy, k is boltzmann's constant, and C is Arrhenius constant. To fit this equation, the densification rate was calculated from the slope of the density curve versus sintering time. We then plotted $TD^m (d\rho/dt)$ against reciprocal temperature ($1/T$). This procedure is followed for three densities of 92%, 96%, and 97% for the CeO₂ powder. A curve fitting of the result for different values of m are shown in Fig. 6.5a and b. For both $m = 3$ and 4, data equally fit into the straight line with the almost same R-squared value of 0.8. It was therefore concluded that, Fig. 6.5 cannot determine m nor the sintering mechanism of CeO₂ powder by itself. Chen and Chen [78] also approached the same conclusion for the sintering mechanism of nano CeO₂ powder, and finally they accepted sintering mechanism of grain boundary diffusion, $m = 4$, which had the nearest value of activation energy to that of grain growth mechanism. However, densification and grain growth may be carried out under different diffusion mechanisms, and it seems to be not necessary to reveal the same values of activation energies for both mechanisms.

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Note that, some data in Fig. 6.5 deviate from the fitted straight line suggesting that $f(\rho)$ is not independent of ρ in the range of densities reported here, and therefore, the straight line fitting of data in order to investigate the dominant mechanism of sintering may not be very accurate. This finding is in contrast with the calculations by Chen and Chen [78] and Hansen [134] who revealed density independent of $f(\rho)$ in the range of 60-90%.

Fig. 6.5. Size compensated densification rate versus reciprocal temperature, with $m = 3$ (a), and 4 (b) for CeO₂ at the various densities of 92%, 96%, and 97%.

The activation energies of sintering implied by the slopes of plots 6.5 were 1144.00 and 932.11 kJ/mol for the m values of 3 and 4, respectively. Chen and Chen [78] reported smaller activation energies of 535 ($m = 3$) and 387 ($m = 4$) kJ/mol for sintering of nano ceria powder. Smaller activation energy obtained for densification of nano powder, same as that of particle growth mechanism can be attributed to the larger surface area of nano powder which enhances the atomic diffusion and facilitates the densification of nano samples.

6.4. Sintering Behavior and Grain Growth of Y₂O₃-doped CeO₂

Fig. 6.6 shows the XRD results of PC and YC (0.25, 0.5, 1.5, and 8 mol% yttria-doped ceria) samples sintered at 1550°C without applying any sintering time. All the samples were found to have the CeO₂ fluorite structure by comparing with the standard X-ray diffraction patterns. The (111) XRD peaks were slightly shifted to the smaller angles with increase of yttria concentration up to 0.5 mol%. Such a decrease can be attributed to the substitution of larger Y³⁺ ions ($r = 0.102$ nm) for Ce⁴⁺ ions in the cubic lattice structure of CeO₂ [92]. For the higher concentrations of additive (1.5 and 8 mol% YC samples), the peaks shifted to the bigger angles. This is probably because of precipitation of yttria in the ceria matrix (exceeding the solubility limit) that causes large distortion of the crystal structure due to the large difference of ionic radiuses. It is noteworthy that, not any regular trend of peak angles was found for the yttria-doped ceria powders. This may indicate the presence of yttria as a second phase, not solute, in the ceria powder before any sintering process.

Fig. 6.6. XRD plot of 0, 0.25, 0.5, 1.5, and 8 mol% Y₂O₃-doped CeO₂ samples sintered at 1550°C. Inset: Magnified (111) characteristic peaks of mentioned samples around $2\theta \approx 28.7^\circ$.

Fig. 6.7. Relative density of Y₂O₃-doped CeO₂ as a function of dopant concentration at various sintering temperatures.

Effect of yttria concentration on the sinterability of ceria powders sintered at 1550°C and 1700°C is shown in Fig. 6.7. Relative density of samples sintered at 1550°C increased with increase of yttria concentration up to 0.5 mol%, and then decreased for the higher additive concentrations.

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According to the XRD results (Fig. 6.6) of Y₂O₃-doped samples sintered at 1550°C, Y₂O₃ dopants with the concentrations lesser than 0.5 mol% dissolved in the CeO₂ matrix. Dissolution of Y³⁺ ions in the ceria crystal structure would result in the formation of oxygen vacancy according to Kroger-Vink notation [72],

Since interstitial cation diffusion is rate limiting mechanism in the ceria based materials, increase of oxygen vacancy (V_o'') would result in the formation of interstitial cerium (Ce_i^{***}) and enhancement of ionic diffusivity and sinterability of samples as well [70],

$$[Ce_i^{***}] = [V_o''] \frac{k_F}{k_S} \exp\left(-\frac{\Delta G_F - \Delta G_S}{kT}\right) \quad \text{Eq (6.7)}$$

where k_F and k_S are the temperature-independent constant, and ΔG_F and ΔG_S refer to Frenkel and Schottky defect formation.

Sharp decrease in the relative densities at the higher yttria concentrations e.g., samples 1.5YC (82.00%) and 8YC (76.50%) sintered at 1550°C can be attributed to the distortion of ceria lattice structure due to exceeding of the solubility limit and precipitation of yttria with the larger atomic radius in the ceria matrix [94].

The relative density of YC samples sintered at 1700°C increased consistently with increase of Y₂O₃ concentration. This can be attributed to the dissolution of yttria molecules or the faster atomic diffusion at the higher temperatures, which can supersede the deteriorating effect of lattice distortion at the higher yttria concentrations. However increase of yttria concentration up to 8 mol% resulted in the presence of micro cracks and a slight decrease in the relative density at this sintering temperature. Nearly full density of 99.99 % was obtained for the 1.5YC sample sintered at 1700°C.

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Fig. 6.8 shows the effect of yttria concentration on the grain size of samples sintered at 1550°C and 1700°C. Grain size of YC samples sintered at 1550°C consistently decreased with the yttria concentration. This can be attributed to the solute drag effect [70] or Zener effect of second phase [128], which would suppress grain boundary mobility and grain growth of samples as a result. At the higher sintering temperature of 1700°C grain size increased slightly up to 0.5 mol% doping, and then decreased sharply. The increment in the grain size can be attributed to the higher solubility of yttria at the higher temperature, which would result in the formation of oxygen vacancies and increase of ionic diffusion and grain size as a result. 1% addition of yttria (YC1.5) resulted in the sharp decrease of grain size probably due to the activation of solute drag [70] or Zener effect [128] mechanisms at the higher yttria concentrations. Effect of yttria doping to suppress grain growth is obvious from the SEM images of samples PC (98.00%, 26.4 μm) and 1.5YC (99.99%, 10.7 μm) sintered at 1700°C (Fig. 6.9a and b).

Fig. 6.8. Post-sintering grain size of Y₂O₃-doped CeO₂ as a function of dopant concentration at various sintering temperatures.

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Fig.6.9. SEM images of (a) undoped CeO₂ sintered at 1700°C (26.4 μm, 98.00%); (b) 1.5 mol% Y₂O₃-doped CeO₂ sintered at 1700°C (10.7 μm, 99.99%); and (c) 0.5 mol% Y₂O₃-doped CeO₂ sintered at 1550°C (2.5 μm, 98.50%).

Considering the results of Fig. 6.7 and Fig. 6.8, it can be deduced that higher amounts of yttria doping are preferential at the higher sintering temperatures due to the significant effect of yttria on suppressing the grain growth while not deteriorating the relative density, whereas an optimum amount of yttria should be defined at the lower sintering temperatures in order to obtain both advantages of smaller grain sizes and higher degree of relative densities. However, it should be considered that formation of macro cracks for the higher amounts of yttria doping needs further studies.

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In the optimum condition, high relative densities of 98.50% and 99.99% with grain sizes of 2.5 and 10.7 μm were obtained for the 0.5YC and 1.5YC samples sintered at 1550°C and 1700°C, respectively. The grain size obtained for sample 0.5YC is smaller than a reported value of 6 μm for the 3% yttria-doped ceria with a same relative density of 98.5% [76]. Avoiding ball milling of admixture of primary powders in order to keep yttria as a second phase (to enhance pinning effect) in the ceria matrix may be responsible for the smaller grain size obtained here. However, these two samples revealed large grain size distributions (Fig. 6.9b and c) for example, the grain size of 1.5YC sample sintered at 1700°C ranged from 3.2 to 14.7 μm .

It is noteworthy that, generally sintering dopants affect the grain size of ceria matrix undesirably in a way similar to their effect on density [93, 94]. However, yttria doping here decreased the grain size of YC samples sintered at 1550°C (up to 0.5 mol % yttria) and 1700°C, and also slightly enhanced the densification process. This can be attributed to the effect of Y₂O₃ as a second phase in the CeO₂ matrix, which would suppress the grain growth due to the pinning effect, and also increase the density due to the gradual dissolution of Y₂O₃ in CeO₂ while sintering.

In general, the effect of Y₂O₃ doping on the relative density and grain size of samples can be summarized as follows: i) yttria dissolution in the ceria matrix increases the ionic diffusivity, and grain size and relative density as a result. ii) yttria precipitation on the grain boundaries (due to solute drag effect or exceeding solubility limit) would result in decrease of both grain size and density. The resultant of these opposing forces, therefore, would define the final grain size and relative density of samples. In the best case, partial yttria dissolution to increase density and yttria precipitation to decrease grain size may affect paralleling (e.g. at 1550°C up to 0.5 mol % yttria doping).

6.5. Conclusions

- i. Higher sintering temperatures promoted the isothermal densification process, but it undesirably resulted in the significant grain growth of undoped CeO₂ samples. However, samples sintered at 1350°C and 1450°C relatively had both advantages of higher relative density and smaller grain size. In the optimum condition, the relative densities of 97.60% and 98.23%, and the grain sizes of 1.1 and 14.2 μm were obtained for the samples sintered at 1350°C and 1450°C for sintering times of 8 and 10 hr, respectively.
- ii. Since the grain growth data fitted well by all the exponent (n) values of 2, 3 and 4 proposed by the various classical grain growth kinetics models, the exact grain growth mechanism of CeO₂ could not be defined here. However, samples sintered at the higher sintering temperatures of 1450°C and 1550°C revealed smaller deviation from the fitted trend line for n value of 2 which indicates the cross-grain-boundary diffusion growth mechanism.
- iii. The sintering data were equally straight line fitted for the both m values of 3 and 4 proposed by Herring's law for the bulk and grain-boundary-diffusion control, respectively. It was therefore concluded that, the fitting result cannot determine m nor the sintering mechanism of CeO₂ powder by itself. The sintering activation energies of 1144.00 and 932.11 kJ/mol were obtained for the m values of 3 and 4, respectively.

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- iv. In general, increase of yttria concentration enhanced the sinterability slightly, but it significantly suppressed the grain growth of samples. In the optimum condition, high relative densities of 98.50% and 99.99% with grain sizes of 2.5 and 10.7 μm were obtained for the 0.5 mol% and 1.5% yttria-doped samples sintered at 1550°C and 1700°C, respectively.

Chapter 7: Mechanical Properties of Y₂O₃-doped Ceria Powder

7.1. Introduction

Compared to the mostly common used solid electrolytes in SOFCs applications, such as ZrO₂-based materials CeO₂ has a higher electrical conductivity at lower operating temperatures [79]. However, CeO₂-based materials have weaker mechanical properties, and are very susceptible to fail and fracture during fabrication and operation. The following chapter investigates indentation behavior of CeO₂, and reveals the effects of various parameters, such as Y₂O₃ doping, density, and grain size on the mechanical properties of CeO₂ material obtained via nano/micro indentation technique.

7.2. Effect of Y₂O₃ Doping on Nano Hardness and Vickers Hardness of CeO₂

It is now generally accepted that the indentation hardness increases with decrease of indentation force (indentation size effect (ISE)) [62, 105, 134]. In order to obtain a complete understanding of indentation phenomena over a wider range of applied test load and also to compare the present results with other studies, we investigated the indentation properties of samples at the various loads of 2 and 50 mN (nano range), and 0.25 N (micro range).

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As it is expected, the nano hardness results were larger than the micro hardness. The main reason can be explained as the analysis of the nano indentation hardness using the projected contact area at the peak load instead of the projected area, as well as the purely elastic contact assumption describing the elastic\plastic indentation process [107].

Surface roughness is the other factor that can affect the hardness of materials especially at the nano ranges of indentation load [135]. The attempt was made in this work to achieve the same surface roughness by polishing down the samples up to 1 μm diamond paste. However, according to AFM images, the surface roughness itself depended on the relative density of samples, e.g. sample YC1.5, 1700°C with the maximum density of 99.99% showed the smoothest surface morphology with the average surface-roughness (R_a) value of 3.02 nm, whereas sample YC8, 1550°C with a smaller relative density of 76.50% revealed the rougher surface morphology with R_a value of 24.00 nm (Fig. 7.1a and b). According to Kim study [126], the surface roughness does not have any significant effect on the measured hardness at the indentation loads larger than 20 mN. So, the effect of roughness here can be ignored for the hardness values measured at 50 mN and 0.25 N loading.

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Fig. 7.1. Surface morphologies and average surface-roughness, R_a , reassured by AFM for samples (a)YC1.5, 1700°C (99.99%) and (b)YC8, 1550°C (76.50%).

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Effect of yttria doping on nano and Vickers hardness of YC samples sintered at 1550°C is shown in Fig. 7.2. In general, both nano and Vickers harnesses increased with the increase of yttria doping up to 0.5 mol%, and then decreased for further amounts of doping irrespective of the various loads used to measure the hardness. This can be attributed to the superseding effect of density (Fig. 6.7) than yttria doping on the hardness (Fig. 7.2) of samples. Sample 8YC sintered at 1550°C with a lowest relative density of 76.50% had the minimum H_V of 2.1 GPa, and H_n of 10.3 and 3.8 GPa at 2 and 50 mN loading respectively, whereas in the same condition, larger H_V of 5.6, and H_n of 24.7 and 11.6 GPa were obtained for 0.51YC sample which had a maximum relative density of 98.50%.

Fig.7.2. Nano and Micro hardness of Y₂O₃-doped CeO₂ sintered at 1550°C as a function of dopant concentration.

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Samples sintered at 1700°C had the larger hardness values than the ones sintered at 1550°C due to their higher relative densities (Table 7.1). The 1.5YC sample ($\rho = 99.99\%$), sintered at 1700°C had the largest H_V of 8.9, and H_n of 55.0 and 15.5 GPa at the various loads of 2 and 50 mN, respectively. These results are higher than the H_n of 9 GPa ($\rho = 94\%$) at 5 mN loading and H_V of 3.9 GPa ($\rho = 94\%$) at 20 N loading, which are reported for undoped ceria [102, 109]. H_n value of 55.0 obtained for 1.5YC, 1700°C at 2 mN loading is also much higher than the reported H_n of 18.3 GPa for yttria-doped zirconia at 1 mN loading [106]. Effect of density on hardness was also obvious from the result of PC samples sintered at 1550°C for 0, 8, and 14 hr (Table 7.1). In general, these samples were harder when compared to the samples 1.5 YC, 1550°C and 8YC, 1550°C, which had lower relative densities.

Table 7.1. Mechanical properties of undoped and yttria-doped ceria samples sintered at 1550°C and 1700°C.

Sample Name	Relative Density %	Grain Size (μm)	Modulus (GPa)		Nano Hardness H_n (GPa)		Vickers Hardness (GPa)	Fracture Toughness MPa.m ^{1/2}	Remarks
			2 mN	50 mN	2 mN	50 mN	250 mN		
PC	98.00	26.4	686.8	371.5	39.7	13.0	7.7	5.1	$T_s = 1700^\circ\text{C}$ $t_s = 0$ hr
1.5YC	99.99	10.7	964.0	389.0	55.0	15.5	8.9	3.4	
PC 0 hr	96.13	7.1	451.0	252.0	23.0	9.3	5.3	3.9	$T_s = 1550^\circ\text{C}$ $t_s = 0, 8 \text{ \& } 14$ hr
PC 8 hr	97.50	37.0	464.3	287.3	23.8	10.3	5.2	3.7	
PC 14 hr	98.30	34.0	390.5	284.2	19.1	10.4	4.6	4.2	

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To study effect of second phase or solid solution strengthening on the hardness of ceria, the yttria concentration was sharply increased to 8%, but as it is seen from Fig. 7.2, the hardness decreased for the 8YC sample sintered at 1550°C. According to literature [60-62], grain size is the other important factor that can affect hardness of both cubic and non-cubic ceramic materials. However, due to the superseding effect of density on the hardness, this trend was not obvious here for the YC samples at the sintering temperature of 1550°C

Considering the relative density (Fig. 6.7) and hardness (Fig. 7.2) results of YC samples sintered at 1550°C, it can be concluded that density rather than yttria concentration or grain size (Fig. 6.8) was the most important factor that affected the hardness of ceria. The direct effect of density on the hardness of ceria samples is also obvious from the load displacement curves of YC0.5 (98.50%) and YC8 (76.50%) samples sintered at 1550°C, and YC1.5 (99.99%) sample sintered at 1700°C (Fig. 7.3). Compared to YC1.5 and YC0.5, the YC8 sample showed the larger indentation depth due to its smaller relative density. In fact, the atomic movement is much easier at the lower densities due to the higher degree of porosities or free space inside the material, so for the constant indentation load, the indentation depth increases and the hardness conclusively decreases with increase of density. The direct effect of density (or inverse effect of porosity) on the hardness of ceramics also has been reported by some others [112, 136, 137].

Fig. 7.3. Load-displacement curves of samples YC0.5 (98.50%) and YC8 (76.50%) sintered at 1550°C, and YC1.5 (99.99%) sintered at 1700°C illustrated by nano indentation testing.

7.3. Effect of Y₂O₃ Doping on the Elastic Properties of CeO₂

The same effect of density on the hardness was observed for the elastic modulus (*E*) of samples sintered at 1550°C and 1700°C (Table 7.1 and Fig. 7.4). Sample 1.5YC sintered at 1700°C with a nearly full density of 99.99% had the highest *E* value of 964.0 and 389.0 GPa at 2 and 50 mN loading, respectively. These results are higher than the *E* value of 270.0 GPa at 5 mN loading reported by Wang [102] for ceria with a relative density of 94%. Wang also revealed *E* value of 264 GPa for the undoped ceria using the four-point method. This result is near to the *E* values obtained here for the samples with the lower relative densities of 96.00 to 98.00% (Table 7.1).

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Fig. 7.4. Elastic modulus of Y₂O₃-doped CeO₂ sintered at 1550°C as a function of dopant concentration.

There is not any good explanation that clarifies effect of density on the Elastic modulus of samples; this is because the elastic modulus mostly depends on the intrinsic atomic bonding energy rather than the atomic movement. However, some researchers [138, 139] have revealed the effect of porosity on the elastic properties of ceramics. Atkinson et al [138] revealed the decrescent effect of porosity, P , on the elastic modulus of YSZ by the following equation

$$E = E_0 \frac{(1 - P)^2}{(1 + b_E P)} \quad \text{Eq (7.1)}$$

where E_0 and b_E are the equation constants.

Wang [103] has reported the reciprocal effect of oxygen vacancy on the elastic modulus of ceria due to the expansion of Ce-O bond length. But as it is obvious from Fig. 7.4, this theory cannot be applicable here (E values didn't decrease with ytria concentration), and the effect of oxygen vacancy due to ytria doping seems to be negligible.

7.4. Effect of Y₂O₃ Doping on the Fracture Toughness of CeO₂

The fracture toughness (K_{IC}) results at 20 N loading are shown in Fig. 7.5 and Table 7.1. In general, K_{IC} increased with the decrease of hardness and density e.g., sample 1.5YC, 1700°C with the maximum hardness and density had a low K_{IC} of 3.4 MPa.m^{1/2}. In the optimum condition, the K_{IC} of 5.1 MPa.m^{1/2}, H_V of 7.7 GPa, and H_n of 13.0 GPa (at 50 mN loading) were obtained for the PC sample ($\rho = 98\%$) sintered at 1700°C. The K_{IC} value obtained here was larger than the reported K_{IC} of 1 to 2 MPa.m^{1/2} for the undoped ceria [80, 109]. This can be attributed to the different methods or different values of E were used to measure K_{IC} . In other hands, this higher value can be attributed to the lesser processing defects of sample.

Fig. 7.5. Fracture toughness and Vickers hardness CeO₂ at 20 N loading as a function of Y₂O₃ doping.

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Here, the attempt will be made to interpret the reciprocal effect of density on the fracture toughness shown by this work. The basic equation for the fracture toughness of ceramics can be expressed as Eq. 7.2 [82]

$$K_{IC} = \sqrt{EG_c} \quad \text{Eq (7.2)}$$

where E is the elastic modulus, and G_c is known as a critical elastic energy release rate. The effect of density on K_{IC} can be explained by micro crack formation and extension, or deflection toughening (in the case of larger fraction of porosity) mechanisms [82]. Briefly, these mechanisms explain that, presence of any micro crack, defect, or porosity inside the material would result in increase of G_c or strain energy release rate by extension of micro cracks and redistribution of stress ahead of the crack tip or by modifying the crack path. Conclusively, increase of density, which would result in the decrease of porosity or defect fraction inside the material, would decrease G_c and K_{IC} as a result. However, increase of density will also result in increase of hardness and elastic modulus, and this will oppositely induce the K_{IC} to increase.

The various effects of density and elastic modulus on K_{IC} can be explained better by considering the results of YC samples sintered at 1550°C (Fig. 4 and 5). In both stages -before and after 0.5 mol% Y₂O₃ doping- K_{IC} reciprocally increased or decreased with the density, and hardness. It is therefore concluded that the reciprocal effect of ρ , and H on G_c and K_{IC} (dominant effect of crack deflection mechanism) superseded the direct effect of E. The superseding effect of G_c than E on the fracture toughness of undoped ceria is also reported by Wang et al [82].

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Fig. 7.6. Vickers indentation images of samples (a) YC0.5 (98.50%) and (b) YC8 (76.50%) sintered at 1550°C.

Effect of crack deflection mechanism to improve the fracture toughness of samples is also evident from the micro indentation image of samples YC0.5 (98.50%) and YC8 (76.50%) sintered at 1550°C (Fig. 7.6a and b). The crack observed at the corner of YC8 projection is quite sharp and straight, whereas the crack exhibits in the YC8 indentation is propagated and deflected multiple times due to the interaction of micro crack with the porosity inside the sample with the smaller relative density.

According to the literature [60, 63], decrease in the grain size will result in improvement of fracture toughness by activating the crack deflection mechanism at the grain boundaries. However, not any significant effect of grain size on K_{IC} was observed in this work; this is because density superceded the effects of other parameters. The effect of yttria doping to increase K_{IC} due to the introduction of oxygen vacancy [82] also can be negligible here.

7.5. Conclusions

- i. Density rather than the Y₂O₃ concentration or grain size was the most important factor that affected hardness, toughness, and the elastic modulus of CeO₂ samples.
- ii. Increase of density resulted in the increase of nano hardness (H_n), and Vickers hardness (H_v), and elastic modulus (E) as well. The largest H_v of 8.9 GPa, H_n of 15.7 GPa, and E of 389.0 MPa were obtained for the 1.5 mol% Y₂O₃-doped sample with a nearly full density of 99.99%.
- iii. The larger fracture toughness (K_{IC}) results were obtained for the lesser densified samples due to the increase of porosity and activation of micro crack formation or deflection mechanism at the smaller densities.

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- iv. In the optimum condition, K_{IC} of 5.1 MPa.m^{1/2}, H_V of 7.7 GPa, H_n of 13.0 GPa, and E of 371.5 GPa were obtained for the undoped CeO₂ sample (ρ = 98%) sintered at 1700°C.

Chapter 8: Conclusions

8.1. Synthesis and Growth Kinetics of Nano CeO₂

Powder

Nano cerium (IV) oxide powder was prepared via homogeneous precipitation method using cerium nitrate and HMT as the reactant materials. The main conclusions can be summarized as follows:

- i. Increase of both cerium nitrate and HMT concentration resulted in spherical particles' morphology, e.g. a nearly hexagonal or spherical particles were obtained for sample A (0.3 mol/l cerium nitrate-1.5 mol/l HMT) with the highest degree of reactants concentration synthesized at 40°C for 5 hr.
- ii. Increase of particles size led to formation of more faceted particles due to the faster growth of particles along {111} surfaces. A faceted particle of 17.0 nm was obtained from sample D (0.1 mol/l cerium nitrate-1mol/l HMT) synthesized at 40°C for 48 hr.
- iii. Different particle sizes of 8.5 to 68.2 nm were produced under various experimental conditions. It was observed that, degree of saturation was the most important factor that affected particle sizes of synthesized nano ceria powder. Degree of saturation itself depended on the various experimental parameters, such as reactants concentration, reaction time and reaction temperature.

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- iv. In general, the particle sizes increased with the increase of reaction time and reaction temperature due to the increase of ceria concentration or saturation.
- v. Increase of HMT concentration initially increased the particle size then decreased it; it was therefore concluded that, not only the reactant concentration but also the HMT to cerium nitrate molar ratio (R) affects saturation and particle size as a result. Increase of cerium nitrate concentration consistently increased the particle size.
- vi. In general, less agglomerated powders with the better properties were obtained for the R values around 5.
- vii. Degree of yield percentage increased with the reaction temperature. In the optimum condition, an acceptable yield of 75% and a particle size of 41 nm were obtained for sample D (0.1 mol/l cerium nitrate-1mol/l HMT) synthesized at 40°C for 96 hr.
- viii. It was observed that, with the increase of reactants concentration the grain growth mechanism changed from Ostwald ripening to an oriented attachment mechanism due to the increase of ceria concentration or saturation.
- ix. By plotting $\ln(k)$ versus $1/T$, small activation energy of 9.06 kJ was obtained for the particle growth of sample D (0.1 mol/l cerium nitrate-1mol/l HMT) via Ostwald ripening mechanism.

8.2. Sintering and Mechanical Properties of Undoped and Y₂O₃-doped CeO₂ Powder

The undoped and Y₂O₃-doped CeO₂ powders were isothermally sintered at the different temperatures and for the various times. The nano hardness and the elastic modulus of sintered samples were measured via nano indentation technique. Micro indentation method was applied to measure the Vickers hardness and the fracture toughness of samples. The main conclusions are summarized as follows:

- i. Higher sintering temperatures promoted the isothermal densification process, but it undesirably resulted in the significant grain growth of undoped CeO₂ samples. However, samples sintered at 1350°C and 1450°C relatively had both advantageous of higher relative density and smaller grain size. In the optimum condition, the relative densities of 97.60% and 98.23%, and the grain sizes of 1.06 and 14.21 μm were obtained for the samples sintered at 1350°C and 1450°C for sintering times of 8 and 10 hr, respectively.
- ii. Since the grain growth data fitted well by all the exponent (n) values of 2, 3 and 4, proposed by the various classical grain growth kinetics models, the exact grain growth mechanism of CeO₂ could not be defined here. However, samples sintered at the higher sintering temperatures of 1450°C and 1550°C revealed smaller deviation from the fitted trend line for n value of 2 which indicates the cross-grain-boundary diffusion growth mechanism.
- iii. The sintering data were equally straight line fitted for the both m values of 3, and 4 proposed by Herring's law for the bulk and grain-boundary-diffusion control, respectively. It was therefore concluded that, the fitting result cannot determine m nor the sintering mechanism of CeO₂ powder by

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itself. The sintering activation energies of 1144.00 and 932.11 kJ/mol were obtained for the m values of 3 and 4, respectively.

- iv. In general, increase of yttria concentration enhanced the sinterability slightly, but it significantly suppressed the grain growth of samples. In the optimum condition, high relative densities of 98.50% and 99.99% with the grain sizes of 2.5 and 10.7 μm were obtained for the 0.5 and 1.5 mol% yttria-doped samples sintered at 1550°C and 1700°C, respectively.
- v. Density rather than the Y₂O₃ concentration or grain size was the most important factor that affected hardness, toughness, and the elastic modulus of CeO₂.
- vi. Increase of density resulted in the increase of nano hardness (H_n), Vickers hardness (H_v), and elastic modulus (E) as well. The largest H_v of 8.9 GPa, H_n of 15.7 GPa, and E of 389.0 MPa were obtained for the 1.5 mol% Y₂O₃-doped sample with a nearly full density of 99.99%.
- vii. The larger fracture toughness (K_{IC}) results were obtained for the lesser densified samples due to the increase of porosity and activation of micro crack formation or deflection mechanism at the smaller densities.
- viii. In the optimum condition, K_{IC} of 5.1 MPa.m^{1/2}, H_v of 7.7 GPa, H_n of 13.0 GPa, and E of 371.5 GPa were obtained for the undoped CeO₂ sample (ρ = 98%) sintered at 1700°C.

Chapter 9: Suggestions for Further Studies

9.1. Synthesis and Growth Kinetics of Nano CeO₂ Powder

- **Using mixture of water and alcohol as a solvent**

According to the particle analyzer results, the synthesized nano ceria powders were agglomerated and formed the secondary particles with sizes around 100 nm. In order to reduce the agglomeration size, various approaches such as using surfactant or using mixture of water and alcohol as a solvent are recommended [83, 84]. This is because; the long molecular chains of surfactant or alcohol cover the surface of particles and prohibit the outer-layer atomic attachments.

- **Defining the exact value of optimum HMT to cerium nitrate ratio (R value)**

As it was observed in this work, the amount of HMT to cerium nitrate ratio (R value)

has a significant effect on the quality of synthesized ceria powder. Increase in R would result in incomplete dehydration or agglomeration of ceria powder. On the other hand, decrease in R would undesirably decrease the yield percentage of reactions. The optimum R value of 15 obtained in the present work is far from the R value of 3 reported for Ce³⁺-NH₄⁺ system [120]. However, further studies are required to define the exact critical R value.

9.2. Sintering and Mechanical Properties of Undoped and Y₂O₃-doped CeO₂ Powder

- **Investigating formation of Ce₂O₃ material at the higher sintering temperatures**

CeO₂ has bufferic properties, and it can easily reduce to Ce₂O₃ via activation of diffusional mechanisms. Higher sintering temperatures would facilitate this transformation by speeding up oxygen and cerium atomic diffusion, and would result in formation of Ce₂O₃ material which has different properties, and has a lower theoretical density compared to CeO₂. Therefore, the X-ray Photoelectron Spectroscopy (XPS) or X-ray Diffraction (XRD) analyses are necessary to define the exact amount of Ce₂O₃ and to determine the exact relative densities of sintered samples as well.

- **Investigating formation of oxygen vacancy or Ce₂O₃ material in the Y₂O₃-doped CeO₂**

According to Kroger-Vink reaction [72], substitution of Y³⁺ ion for Ce³⁺ ion in the Y₂O₃-doped CeO₂ crystal structure would result in the formation of oxygen vacancy or sometimes stoichiometric phase of Ce₂O₃. Therefore, in order to define the exact amount of relative density, XRD and XPS analyses of Y₂O₃-doped CeO₂ samples are also necessary here.

- **Investigating individual effects of second phase, oxygen vacancy, and grain size on the micro/nano indentation properties of undoped or Y₂O₃-doped CeO₂ samples**

As it was observed in this work, yttria doping led to simultaneous change of grain size and relative density of samples. According to literature [72], yttria doping can also result in formation of oxygen vacancy and second phase of

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Ce₂O₃ or Y₂O₃ (when yttria does not entirely dissolve in ceria matrix) inside the ceria matrix. All these parameters –grain size, density, oxygen vacancy, and second phase- can individually affect the mechanical properties of ceria matrix, but as it was observed in this work density is the strongest one which supercedes the effects of other parameters. Therefore, in order to understand the effects of other parameters, such as grain size, oxygen vacancy, and second phase on mechanical properties of CeO₂, it is recommended for further studies to investigate the effect of yttria doping for the “constant value of relative density”.

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