CHAPTER 2
SYNTHESIS OF RARE-EARTHS DOPED CERIA (RE$^{3+}$:CeO$_2$) NANOPowDERS BY CITRATE NITRATE AUTO-COMBUSTION

2.1. INTRODUCTION

Traditionally, the word ceramics is associated with clay-based products such as bricks, tiles, pottery, tableware, sanitaryware and glasses. Naturally occurring minerals like sand, quartz, bauxite, feldspar etc., are used in the manufacture of these materials. Advanced ceramics differ from conventional ceramics in their high-mechanical strength, fracture toughness, wear resistance, refractory, dielectric, magnetic and optical properties. Advanced ceramics or fine ceramics are high value-added inorganic materials produced from high purity synthetic powders to control microstructure and properties. Wet-chemical routes (Segel et al., 1979) e.g., co-precipitation, sol-gel, spray-dry, freeze-dry etc., are usually employed to prepare advanced ceramic powders having submicron size, narrow size distribution and absence of particle agglomerates. However, these methods are quite involved; require long processing time, costly chemicals and special equipment. Therefore, there is a need for an alternative to the wet-chemical methods.

2.2. COMBUSTION SYNTHESIS

Combustion method is an attractive technique for the synthesis of a wide variety of advanced materials, including powders and products of ceramics, inter-metallics, composites, and functionally graded materials. This method was discovered in the former Soviet Union by Merzhanov et al., 1971.
The development of this technique by Merzhanov and co-workers led to the appearance of a new scientific direction that incorporates both aspects of combustion and materials science. At about the same time, some work concerning the combustion aspects of this method was also done in the United States (Booth et al., 1953; Walton et al., 1959; Hardt et al., 1973). However, the full potential of combustion synthesis in the production of advanced materials was not utilized. The scientific and technological activity in the field picked up in the United States during 1980s. The significant results of combustion synthesis have been described in a number of review articles (Munir et al., 1989; Merzhanov et al., 1990; Holt et al., 1991; Rice et al., 1991; Varma et al., 1992; Moore et al., 1995). At the present time, scientists and engineers in many other countries are also involved in research and further development of combustion synthesis, as well as interesting theoretical, experimental and technological results have been reported from various parts of the world (SHS Bibliography, 1996).

Many researchers have attempted to use the heat generated by exothermic chemical reactions in the synthesis of high-temperature ceramic materials. Merzhanov et al., used the exothermic reaction between the elements (metal-fuel, and nonmetal-oxidizer) to produce a host of materials: borides, carbides, carbonitrides, cermets, chalcogenides, hydrides, nitrides, oxides and silicides (Merzhanov et al., 1993). This process, popularly known as self-propagating high-temperature synthesis (SHS), is also called furnaceless or fire synthesis.
Here, we present the results of a modified combustion process (low temperature initiated, self-propagating, gas-producing, exothermic reaction) for the synthesis of ceramics employing redox compounds and mixtures. The term combustion covers smoldering (heterogeneous) flaming (homogeneous gas phase) as well as explosive reactions. The rate of combustion determines the nature of reaction, i.e. decomposition, deflagration or detonation. Synthesis of ceramic oxides is achieved by smoldering and flaming reactions.

2.3 PREPARATION OF OXIDES BY THE COMBUSTION OF REDOX MIXTURES

Redox mixtures like KNO$_3$ + C + S once ignited, undergo self-propagating and gas-producing exothermic decomposition. Similar exothermic reactions of redox mixtures are used in rocket propellants e.g., NH$_4$ClO$_4$-Al-CTPB. These redox mixtures containing metallic ingredients (Mg, Al) are known to offer metal oxides as undesired products of combustion. This phenomenon has now been exploited to actually synthesize metal oxides by the combustion of stoichiometric mixtures of metal nitrates (oxidizer) and urea/hydrazine-based fuels. The stoichiometric composition of the metal nitrate (oxidizer) and fuel redox mixtures was calculated based on the total oxidizing and reducing valency of the oxidizer and the fuel which serve as a numerical coefficient for stoichiometries balance such that the equivalence ratio ($\Phi_e$) is unity, i.e., O/F = 1 and the energy release is maximized (Jain et al., 1981). In propellant chemistry, the species M$^{2+}$, M$^{3+}$, M$^{4+}$, C and H are considered to
be reduced with corresponding valencies +2, +3, +4, +4 and +1. Elemental oxygen is considered to be an oxidizing species with valency -2. The valency of nitrogen is considered to be zero. According to this oxidizing and reducing valencies of the fuels such as urea (CH$_4$N$_2$O, U), carbohydrazide (CH$_6$N$_4$O, CH), tetra formyl tris-azine (C$_4$H$_{16}$N$_6$O$_2$, TFTA), oxalyl dihydrazide (C$_2$H$_6$N$_4$O$_2$, ODH), maleic hydrazide (C$_4$H$_4$N$_2$O$_2$, MH), malonic dihydrazide (C$_3$H$_8$N$_4$O$_2$, MDH) and citric acid (C$_6$H$_8$O$_7$, CA) are +6, +8, +28, +10, +16, +16 and +18 respectively (Patil et al., 1993).

2.4 PREPARATION OF RARE EARTHS DOPED CERIUM OXIDES (RE$^{3+}$:CeO$_2$)

Cerium (IV) dioxide (CeO$_2$, known as ceria) nanoparticles have established much attention because of their many interesting characteristics such as electrical conductivity, unique UV absorption ability due to its band-gap energy of 3.2 eV, high stability at high temperature, high hardness and reactivity (Maensiri et al., 2007; Tsunekawa et al., 2000; Trovarelli et al., 1999). Especially, the combination of ceria with supporting metal oxides, or with various rare-earth dopants, is one of the most important catalysts (Kaspar et al., 1999; Trovarelli et al., 2002). It is regarded as a prototype of redox due to its tendency to lose and adsorb oxygen. This property of ceria is called as the oxygen storage capacity which represents the ability of ceria to shift from Ce$^{4+}$ to Ce$^{3+}$ in reducing atmosphere and from Ce$^{3+}$ to Ce$^{4+}$ under oxidizing conditions with charge compensation facilitated via oxygen vacancies. Thus, CeO$_2$ and CeO$_2$-based materials have been extensively used in
a wide variety of applications such as catalysis (Kaspar et al., 1996; Trovarelli et al., 2002), fuel cells (Steele et al., 2001; Kosinski et al., 2011), optics (Li et al., 2002), gas sensors (Jasinski et al., 2003), UV protection of window glass and lenses, and as an additive in cosmetics (Taga et al., 1997). As an active component of catalysts, it is used for the abatement of CO, NOx, and hydrocarbons from automobile exhaust (Fornasiero et al., 1996), soot removal from diesel fuels (Shimizu et al., 2010), oxidation of hydrocarbons in solid oxide fuel cells (Shao et al., 2005), and CO elimination from hydrogen streams of proton exchange membrane (PEM) fuel cells (Fu et al., 2003).

It is generally accepted that the reactivity of ceria is related to the low redox potential of the Ce\(^{3+}/\text{Ce}^{4+}\) pair and to the high oxygen storage capacity that allow this oxide to store oxygen under oxidizing conditions (Ce\(^{4+}\)) and to release it under reducing conditions, thus creating oxygen vacancies and Ce\(^{3+}\) defects. Nowadays, many efforts have been focused on the preparation of well-defined ceria nanoparticles in such a way to create more oxygen vacancies via doping, growing spherical nanoparticles with moderate particle sizes, enhancement of high surface-area to volume ratio for the stabilization of Ce\(^{3+}\). It was reported that the oxidation state of ceria is always close to 4 under ambient conditions, and there is no stabilization of Ce\(^{3+}\) in smaller ceria nanoparticles (<10 nm) (Paun et al., 2012). The size and size distribution of ceria are important in determining their properties (Spanier et al., 2001). The chemical approach is the main route for synthesis of CeO\(_2\) nanoparticles (Adschiri et al., 2001). It is known that nanoparticles usually have specific
shape, especially when they are small, because a single crystal nanoparticle has to be enclosed by crystallographic facets that have lower energy; a spherical particle usually has higher surface energy due to the presence of high index crystallographic facets (Wang et al., 2003). However, the vital goal of these studies is to develop nanomaterials possessing high surface energy, catalytic action, oxygen storage capacity and stability. Experimental and theoretical studies (Kaspar et al., 1999; Trovarelli et al., 1996; Balducci et al., 1997) have shown that the reducibility of CeO$_2$ can be modified via the introduction of dopant cations such as Zr$^{4+}$, Y$^{3+}$, Sm$^{3+}$, Gd$^{3+}$, etc., in the car. The resulting solid solution facilitates a defective fluorite structure with improved oxygen mobility (Sayle et al., 2002).

### 2.5. SOLUTION COMBUSTION SYNTHESIS

Citrate nitrate auto-combustion (CNA) or Solution combustion synthesis (SCS) is a versatile, simple and rapid process, which allows effective synthesis of a variety of nanosize materials. This process involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., citric acid, urea, glycine, hydrazides, etc.). Depending on the type of the precursors, as well as on the conditions used for the process organization, the SCS may occur as either volume or layer-by-layer propagating combustion modes. This process not only yields nanosize oxide materials, but also allows uniform (homogeneous) doping of trace amounts of rare-earth impurity ions in a single step. In the field of electrocatalysis and power applications, a large number of papers on materials preparation for fuel
cells, supercapacitors, batteries and dye-sensitized solar cells have been published. More specifically, many papers are focused on the synthesis of various materials for application in solid oxide fuel cells (SOFC) and direct methanol fuel cells (DMFC). The present chapter deals with the synthesis of some rare earths doped ceria (RE$_{3+}$:CeO$_2$) nanoparticles by citrate nitrate auto-combustion method at 500 °C in a closed furnace shown in Fig. 2.1.

2.6 EXPERIMENTAL

The procedure for the preparation of RE$_{3+}$:CeO$_2$ is described as follows:
The main host precursor of cerium nitrate hexahydrate Ce(NO$_3$)$_3$·6H$_2$O (Aldrich, 99.999%) with different dopants such as Erbium nitrate Er(NO$_3$)$_3$·5H$_2$O (Aldrich, 99.9%), Neodymium nitrate Nd(NO$_3$)$_3$·6H$_2$O (Aldrich, 99.9%), Praseodymium nitrate Pr(NO$_3$)$_3$·6H$_2$O (Aldrich, 99.99%), Yttrium nitrate Y(NO$_3$)$_3$·6H$_2$O (Aldrich, 99.9%), Lanthanum nitrate [La(NO$_3$)$_3$·6H$_2$O], Scandium nitrate [Sc(NO$_3$)$_3$·H$_2$O] and Ytterbium nitrate [Yb(NO$_3$)$_3$·5H$_2$O] were used for the synthesis of each combination of doping in the ratio of 90 : 10 mol%. For the chemical reaction (combustion), the citric acid anhydrous C$_6$H$_8$O$_7$ (Sigma-Aldrich, 99.5%) of suitable quantities were used as a fuel, according to the balanced calculation from the concepts of propellant chemistry (Patil et al., 1993). Stoichiometric amounts of cerium nitrate with respective rare earth chemical were mixed together and dissolved in suitable quantity of de-ionized water. Then the calculated amount of citric acid was also mixed in the solution and stirred mechanically for 2 hours at 60 °C to get a clear and homogeneous solution.
Fig. 2.1 Closed furnace for the combustion synthesis.
Fig. 2.2 The nanopowders and compacts of $\text{RE}^{3+}:\text{CeO}_2$ prepared according to the experimental procedure.
The reaction mixture was transferred to a platinum or alumina crucible, and it was kept inside a preheated furnace at a temperature of 500 ºC. Once the reaction mixture reached the point of spontaneous combustion, it starts burning vigorously. The gaseous volatile molecules such as N₂, CO₂, H₂O and other forms of gaseous products were released during the combustion reaction. Finally, porous solid foam of nanoparticles were obtained in a time span of 10 minutes. The assumed combustion reactions involved among cerium nitrate and fuel (citric acid) with different rare earth nitrate chemicals (nitrates of Er, Nd, Pr, Y, La, Sc and Yb viz.) are given in Table 2.1.

The nanoparticles of Erbium doped ceria (Er³⁺: CeO₂), Praseodymium doped ceria (Pr³⁺:CeO₂), Neodymium doped ceria (Nd³⁺:CeO₂), Lanthanum doped ceria (La³⁺:CeO₂), Scandium doped ceria (Sc³⁺:CeO₂), Ytterbium doped ceria (Yb³⁺:CeO₂) and Yttrium doped ceria (Y³⁺:CeO₂) were synthesized by solution combustion method. The nanopowders and cylindrical compacts are shown in Fig.2.3. Then, the as-combusted foams were collected and converted to powders by smooth grinding. The same process was repeated with different dopants. The as-prepared ceria powders of different rare earth elements were calcined at 700 ºC for 2 hours (at a heating rate of 5 ºC/minute). The calcined RE³⁺:CeO₂ powders were converted into cylindrical compacts by uni-axial compression (Fig. 2.4) with subsequent sintering at 1200 ºC for 6 hrs, at a heating rate of 5 ºC/ min. The schematic diagram for the preparation of RE³⁺:CeO₂ is shown in Fig. 2.5.
Table 2.1 Chemical reactions during the combustion synthesis.

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<th>Equation</th>
<th>Reaction Product</th>
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<td>0.9 ([\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.1 [\text{Er(NO}_3)_3 \cdot 5\text{H}_2\text{O}] + 0.783 [\text{C}_6\text{H}_8\text{O}_7])</td>
<td>(-\Delta \rightarrow \text{(exo) Ce}<em>{0.9}\text{Er}</em>{0.1}\text{O}_{1.95} + \text{organic gas ↑})</td>
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<td>0.9 ([\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.1 [\text{Nd(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.783 [\text{C}_6\text{H}_8\text{O}_7])</td>
<td>(-\Delta \rightarrow \text{(exo) Ce}<em>{0.9}\text{Nd}</em>{0.1}\text{O}_{1.95} + \text{organic gas ↑})</td>
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<td>0.9 ([\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.1 [\text{Pr(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.783 [\text{C}_6\text{H}_8\text{O}_7])</td>
<td>(-\Delta \rightarrow \text{(exo) Ce}<em>{0.9}\text{Pr}</em>{0.1}\text{O}_{1.95} + \text{organic gas ↑})</td>
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<td>0.9 ([\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.1 [\text{Y(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.783 [\text{C}_6\text{H}_8\text{O}_7])</td>
<td>(-\Delta \rightarrow \text{(exo) Ce}<em>{0.9}\text{Y}</em>{0.1}\text{O}_{1.95} + \text{organic gas ↑})</td>
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<td>0.9 ([\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.1 [\text{La(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.783 [\text{C}_6\text{H}_8\text{O}_7])</td>
<td>(-\Delta \rightarrow \text{(exo) Ce}<em>{0.9}\text{La}</em>{0.1}\text{O}_{1.95} + \text{organic gas ↑})</td>
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<td>0.9 ([\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.1 [\text{Sc(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.783 [\text{C}_6\text{H}_8\text{O}_7])</td>
<td>(-\Delta \rightarrow \text{(exo) Ce}<em>{0.9}\text{Sc}</em>{0.1}\text{O}_{1.95} + \text{organic gas ↑})</td>
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<td>0.9 ([\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}] + 0.1 [\text{Yb(NO}_3)_3 \cdot 5\text{H}_2\text{O}] + 0.783 [\text{C}_6\text{H}_8\text{O}_7])</td>
<td>(-\Delta \rightarrow \text{(exo) Ce}<em>{0.9}\text{Yb}</em>{0.1}\text{O}_{1.95} + \text{organic gas ↑})</td>
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Fig. 2.3 Synthesized nanoparticles and pellets of RE$^{3+}$:CeO$_2$.

Fig. 2.4 Uni-axial auto-compressor for the compact preparation.
Fig. 2.5 Schematic for the preparation of $\text{RE}^{3+}:\text{CeO}_2$ electrolyte.

\[
\text{Ce(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} [0.9 \text{ mol}] + \text{RE (NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} [0.1\text{mol}]
+ \text{HOOC.CH}_2\text{CH(OH)(COOH).CH}_2\text{COOH}
[0.783 \text{ mol according to propellant chemistry}]
\]

i) Added to distilled water
ii) Mechanical stirring (2 h at 60°C)

Homogeneous solution

Spontaneous combustion
+ Yielding solid foam of $\text{Ce}_{0.9}\text{RE}_{0.1}\text{O}_{1.95}$

i) Calcined at 700°C for 2 h
ii) Made into cylindrical compacts
iii) Sintered at 1200°C for 6 h

$\text{Ce}_{0.9}\text{RE}_{0.1}\text{O}_{1.95}$ Electrolyte
2.7 CONCLUSION

In the present investigation, a simple and cost effective citrate nitrate auto-combustion (CNA) method was used for the high-yield synthesis of rare-earth (RE) ions doped ceria (RE$^{3+}$:CeO$_2$) in the form of Ce$_{0.9}$La$_{0.1}$O$_{1.95}$, Ce$_{0.9}$Sc$_{0.1}$O$_{1.95}$, Ce$_{0.9}$Yb$_{0.1}$O$_{1.95}$, Ce$_{0.9}$Er$_{0.1}$O$_{1.95}$, Ce$_{0.9}$Pr$_{0.1}$O$_{1.95}$, Ce$_{0.9}$Nd$_{0.1}$O$_{1.95}$, and Ce$_{0.9}$Y$_{0.1}$O$_{1.95}$ nanoparticles, respectively. Nanoparticles with homogeneous size and chemical distribution were obtained with this method. The as-synthesized powders were calcined at 700 °C and converted into cylindrical compacts by sintering at 1200 °C.

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