Chapter 1

Introduction
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1.1 General Background

Zirconia or zirconium oxide is an important multi-functional transition metal oxide being widely used in variety of applications such as ceramics [1], oxygen and NOx sensor [2] and solid electrolyte [3]. Zirconia is widely used in ceramic technology as refractories, abrasives, glasses and enamels [4]. It has become the ideal medium for applications in photonics due to its excellent mechanical, electrical, thermal, optical and stable photochemical properties [5]. In recent years, zirconia has attracted attention as a catalyst [6-11] and catalyst support [12-20] due to its unique amphoteric character and redox properties [23]. It also works as a photocatalyst [22, 23]. Zirconia, after modifying with sulfate anions, forms sulfated zirconia that possesses super acidity (H_0 < -12) and is a potential catalyst for n-alkane isomerisation at ambient temperature [24]. Zirconia after doping with various bi, tri-valent cations forms stabilized zirconia, which has broad industrial applications such as structural ceramics, refractory materials, biomaterials, catalysts, oxygen and NOx sensors, solid oxide fuel cell electrolyte and semiconductor devices [1-5].

1.2 Occurance and History

Zirconia does not occur in nature as a pure oxide. It occurs in chemically combined form as (I) Zircon (ZrO_2.SiO_2) and as free oxide in (II) Baddeleyite (ZrO_2). Zircon contains 68% of zirconia and rest of silica and Baddeleyite contains small amount of HfO_2, TiO_2 and FeO_2 as impurities. These ores are mined in Australia, Brazil, India, South Africa and the USA [25-27]. Zircon has been announced the oldest rock on earth by the geologist, which formed over 4 billion years ago. Zircon resources exceed 60 million tonnes worldwide. Baddeleyite can be found in igneous rocks containing potassium feldspar and plagioclase; it forms at places that are low in
silica. Because of the refractory nature and stability under diverse conditions, baddeleyite grains, along with zircon, are used for uranium-lead radiometric age determinations in geochronometry [27].

Martin Heinrich Klaproth was the first German chemist who discovered an oxide of a new element in 1789, which was extracted on heating a gemstone with alkali. He named it ‘Zirconia’ (ZrO$_2$), from the Arabic word 'Zargon' meaning ‘gold-colored’. In 1824, a Swedish chemist Jons Jacob Berzelius, isolated the ‘Zirconium’ (Zr) metal itself. In 1950's, Magnesium Elektron Limited (MEL) was the first company to develop zirconium metal commercially by introducing a range of ceramic oxide colors [25-27]. The annual worldwide zirconium production is approximately 900,000 tonnes. It also has a concentration of about 130 mg/kg within the Earth's crust and about 0.026 μg/L in sea water [27]. Zirconia has been detected in the sun and in meteorites; lunar rock samples brought back from several Apollo program missions to the moon have a quite high ZrO$_2$ content relative to terrestrial rocks [27].

Out of these two ores of zirconia, zircon is by far the most widespread but it is less pure and requires a significant amount of processing to yield zirconia. The processing of zirconia involves the separation and removal of undesirable materials and impurities, for example, removal of silica in the case of zircon; and iron, titanium and hafnium oxides from baddeleyite [25,26]. There are several routes to the extraction of zirconia from zircon such as (i) chlorination (ii) alkali oxide decomposition (iii) lime fusion and (iv) plasma dissociation. However, these extraction methods are tedious and multi-steps. Therefore the need of chemical synthesis of pure zirconia at lab and large scale is needed due to its diversified applications. Pure zirconia can be prepared by various methods such as conventional precipitation, sol-gel etc. as described in later section.
1.3. Structure of Zirconia

Pure zirconia has three thermodynamically stable crystalline phases under atmospheric pressure: monoclinic (M) (up to 1170 °C), tetragonal (T) (1170-2370 °C), and cubic (C) (2370-2680 °C). It also has an orthorhombic phase at high-pressure [28,29]. All three crystalline phases have different lattice parameters as shown in Table 1.

Table 1. Crystallographic parameters of different crystalline phases of zirconia [28]

<table>
<thead>
<tr>
<th>Crystalline Phase</th>
<th>Monoclinic</th>
<th>Tetragonal</th>
<th>Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P2/c</td>
<td>P4/nmc</td>
<td>Fm3m</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>a ≠ b ≠ c,</td>
<td>a = b ≠ c,</td>
<td>a = b = c,</td>
</tr>
<tr>
<td></td>
<td>α≠γ ≠90° β=90°</td>
<td>α = β = γ =90°</td>
<td>α = β = γ =90°</td>
</tr>
<tr>
<td></td>
<td>a= 5.146 Å</td>
<td>a= 5.090 Å</td>
<td>a = 5.128 Å</td>
</tr>
<tr>
<td></td>
<td>b= 5.212 Å</td>
<td>c= 5.180 Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c= 5.313 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unit cell</td>
<td>abc</td>
<td>ac</td>
<td>a</td>
</tr>
<tr>
<td>Symmetry</td>
<td>C2h</td>
<td>D4h</td>
<td>O_h</td>
</tr>
</tbody>
</table>

In monoclinic zirconia (Figure 1), Zr\(^{4+}\) has 7-fold coordination. Zr\(^{4+}\) cations are surrounded by a tetrahedron (distorted tetrahedral coordination) with four oxygen atoms and a trigon (planer trigonal coordination) with three oxygen atoms, having three different Zr-O bond lengths. The symmetry lattice for monoclinic is C\(_{2h}\). The structure has the lattice parameters of a=5.146 Å, b=5.212 Å and c=5.313 Å. In tetragonal zirconia (Figure 1), Zr\(^{4+}\) has 8-fold coordination. Zr\(^{4+}\) atoms are centrally located in the tetragonal cells and have a distance of 5.090 Å with four oxygen atoms and another four at 5.180 Å. The symmetry lattice for tetragonal is D\(_{4h}\). In cubic zirconia (Figure 1), Zr\(^{4+}\) has 8-fold coordination. In the cubic unit cell structure the distance between Zr\(^{4+}\) atoms and eight oxygen atoms are equidistant with a lattice
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parameter of \(a=5.128\ \text{Å}\). The symmetry lattice for cubic is \(O_h\). The symmetry for zirconia polymorphs decreases with cubic to tetragonal to monoclinic.

![Figure 1. Pictorial presentation of three crystalline phases of Zirconia [30].](image)

1.4 Stabilized Zirconia

Among the three crystalline phases of zirconia, monoclinic phase is thermodynamically stable at room temperature but it undergoes polymorphic transformation at higher temperature, therefore, is not much useful in high temperature applications. During these lattice transformations, substantial volume change occurs, e.g., \(\sim 2.3\%\) during cubic to tetragonal (C-T) and \(\sim 4.5\%\) during tetragonal to monoclinic (T-M) transformation, leading to extensive cracking in the material, which makes pure monoclinic zirconia unsuitable for high temperature structural and mechanical applications [31]. Therefore, efforts have been made to eliminate these structural changes by stabilizing cubic or tetragonal phase at room temperature, which can be done by two ways:

A) Synthesis of nano-crystalline tetragonal phase of zirconia at room temperature by reducing its size into nano level (< 30 nm). Garvie et al. [32] has shown that tetragonal phase of zirconia stabilizes if the crystallite size is <30 nm. However,
during thermal treatment at higher calcination temperature, the size of tetragonal phase increased from the critical crystallite size, i.e., 30 nm, and phase transformation from tetragonal to monoclinic zirconia occurred. The transformation of crystalline phase of zirconia is reported to depend on various factors such as presence of point defects in zirconia structure generated during dehydroxylation [33], presence of water vapor, which facilitates the transformation at lower temperature [34], presence of both large and small particles in the structure and large particles transform at a lower temperature than small particles [35]. The ceramic tetragonal zirconia polycrystals (TZP) used as implanted femoral heads undergo phase transformation of the surface layers with increasing time of implantation [36].

B) The addition of oxides dopants such as CaO, MgO and Y$_2$O$_3$ stabilizes the metastable cubic and tetragonal lattice structure. These dopants incorporate in the zirconia lattice and disfavored the strained monoclinic phase at room temperature and favored more symmetric metastable cubic and tetragonal lattice structure [37,38]. These metastable cubic and tetragonal phases are analogous to those in pure zirconia. The oxide dopant ions are substituted on Zr$^{4+}$ sites with the formation of oxygen vacancy to retain charge neutrality. These metastable phases have prolonged stability at room temperature with low cation mobility in zirconia lattice and locally ordered oxygen vacancies [39].

1.4.1 Types of Stabilized or doped Zirconia

The type of dopants and their concentration added to zirconia lattice forms two types of stabilized zirconia:

I. **Fully stabilized zirconia (FSZ):** FSZ has single cubic phase without any phase transformation from room temperature to higher temperature. Higher concentration of dopant is normally used to synthesize FSZ. It is useful for
applications such as heating elements, oxygen sensors, fuel cell electrolytes, coatings, structural and wear components, and toughening agents in many ceramic composite [40-42].

II. Partially stabilized zirconia (PSZ): PSZ typically consists of two phases (cubic and tetragonal) or may also have a single phase (either tetragonal or cubic). Lower concentration of dopant is normally used to synthesize PSZ. It is a mixture of zirconia polymorphs, because insufficient or smaller amount of cubic phase-forming oxide (dopant or stabilizer) has been added, therefore, a cubic plus metastable tetragonal ZrO₂ mixture is obtained [43]. A smaller addition of dopant to the pure zirconia will bring its structure either (i) into a mixture of cubic and tetragonal phase at a lower temperature or (ii) tetragonal phase at a higher temperature. PSZ having single tetragonal phase is known as tetragonal zirconia polycrystal (TZP). It is important in mechanical and structural applications. TZP offers superior strength, toughness and wear resistance and thus is used in cutting tools, abrasion wheels etc. [44]. TZP ceramics are very much useful in Arthroplasty and dental branch of medical science due to higher surface hardness and smoothness [45].

1.4.2 Properties of Stabilized Zirconia

Stabilized zirconias are well known as ceramics having excellent mechanical, electrical and thermal properties (Table 2). The oxygen ion bulk conductivity in FSZ is by a factor of two times higher compared to that of PSZ, on the other hand PSZ has superior strength and thermo-mechanical properties [46].

1.4.3 Factors responsible for stabilization of zirconia

Two factors: (i) nature of dopants and (ii) dopant concentration have a significant role in the stabilization of zirconia phase:
Table 2. Comparative properties of FSZ and PSZ.

<table>
<thead>
<tr>
<th>Fully stabilized zirconia</th>
<th>Partially stabilized zirconia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic crystal structure</td>
<td>Cubic/Tetragonal crystal structure</td>
</tr>
<tr>
<td>High oxygen conductivity</td>
<td>Moderate oxygen conductivity</td>
</tr>
<tr>
<td>High strength</td>
<td>Very High strength</td>
</tr>
<tr>
<td>Low fracture toughness</td>
<td>High fracture toughness</td>
</tr>
<tr>
<td>No super plasticity</td>
<td>Super plasticity</td>
</tr>
<tr>
<td>High thermal stability</td>
<td>High thermal stability</td>
</tr>
<tr>
<td>Low thermal conductivity</td>
<td>Low thermal conductivity</td>
</tr>
</tbody>
</table>

1.4.3.1 Dopants

The oxide cations, which have either close ionic radius to Zr$^{4+}$ ionic radius (0.84 Å) and lower valence or smaller size and higher valence, have been commonly used to synthesize stabilized zirconia. Among the various dopants, a series of bi, trivalent oxide of dopants such as Ca$^{2+}$, Ba$^{2+}$, Y$^{3+}$, Sc$^{3+}$ and La$^{3+}$, Ac$^{3+}$ ions have been used to stabilize the tetragonal and cubic phases of ZrO$_2$ (Table 3). Furthermore, the stabilization of tetragonal and cubic phases of ZrO$_2$ using oversized/undersized tetravalent oxide of dopants like Si$^{4+}$, Ce$^{4+}$, Ge$^{4+}$, Sn$^{4+}$, Th$^{4+}$, Ti$^{4+}$, pentavalent ion Nb$^{5+}$, Ta$^{5+}$ and nitrides such as Mg$_3$N$_2$, Si$_3$N$_4$, AlN were also found to be effective in forming cationic network and high-energy surface layer [47-53].

Besides the oxide dopants mentioned in the Table 3 to prepare stabilized zirconia, other cation dopants have also been used to add in stabilized zirconia (Table 4) to achieve certain specific properties. For example, addition of rare earth metal oxides to improve the optical and luminescence properties of stabilized zirconia [54-58] and addition of transition elements to improve the sintering, mechanical and electrical properties of stabilized zirconia [59,60]. The incorporation of these dopants was found to reduce the sintering temperature and increase the ionic conductivity and
density at low temperature than stabilized zirconia. Table 4 shows various co-dopants used to add to stabilized zirconia.

**Table 3.** Various oxide dopants used to synthesize stabilized zirconia and their ionic radius

<table>
<thead>
<tr>
<th>Dopants</th>
<th>Ionic radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr⁴⁺(lattice)</td>
<td>0.84</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.99</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.72</td>
</tr>
<tr>
<td>Y³⁺</td>
<td>1.09</td>
</tr>
<tr>
<td>Sc³⁺</td>
<td>0.75</td>
</tr>
<tr>
<td>Ce⁴⁺</td>
<td>1.03</td>
</tr>
<tr>
<td>Pr⁴⁺</td>
<td>1.01</td>
</tr>
<tr>
<td>Nd⁵⁺</td>
<td>1.00</td>
</tr>
<tr>
<td>Pm⁵⁺</td>
<td>0.98</td>
</tr>
<tr>
<td>Sm⁵⁺</td>
<td>0.96</td>
</tr>
<tr>
<td>Yb⁵⁺</td>
<td>0.86</td>
</tr>
<tr>
<td>Ti⁴⁺</td>
<td>0.61</td>
</tr>
<tr>
<td>Th⁴⁺</td>
<td>1.08</td>
</tr>
<tr>
<td>Nb⁵⁺</td>
<td>0.69</td>
</tr>
<tr>
<td>Th⁵⁺</td>
<td>0.95</td>
</tr>
</tbody>
</table>

**Table 4.** Various co-dopants used to add to stabilized zirconia

<table>
<thead>
<tr>
<th>Stabilized zirconia</th>
<th>Dopants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yttria stabilized zirconia</td>
<td>Al³⁺, Fe³⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ce⁴⁺, Ru⁴⁺</td>
</tr>
<tr>
<td>Calcia stabilized zirconia</td>
<td>Ti⁴⁺</td>
</tr>
<tr>
<td>Ceria stabilized zirconia</td>
<td>Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺</td>
</tr>
</tbody>
</table>
1.4.3.2 Concentration of Dopants

The varied concentrations of various dopants have been studied to prepare FSZ or PSZ as shown in Table 5 [61-65]. The amount of the dopants stabilizes the zirconia fully (FSZ) or partially (PSZ) in metastable cubic and tetragonal phases. Amongst various forms of stabilized zirconia, $Y_2O_3$ stabilized $ZrO_2$ has become one of the most important and widely used high temperature ceramic material due to its high ionic conductivity as well as thermal stability and excellent mechanical properties. Different phases of $ZrO_2$ such as Tetragonal zirconia polycrystals (Y-TZP), Partially yttria stabilized zirconia (Y-PSZ) & Fully yttria stabilized zirconia (F-YSZ) can be prepared by properly adjusting 3, 5 and 8 mol% of $Y_2O_3$ concentration respectively in the lattice of $ZrO_2$ [66]. The fine-grained Y-TZP and Y-PSZ exhibit excellent strength and fracture toughness and F-YSZ exhibit high thermal stability and used in high temperature applications.

Table 5. Various dopants and their concentration to prepare FSZ or PSZ

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Concentration (Mole %)</th>
<th>Fully/partially Stabilized</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>16</td>
<td>FSZ</td>
</tr>
<tr>
<td></td>
<td>8-10</td>
<td>PSZ</td>
</tr>
<tr>
<td>MgO</td>
<td>13-16</td>
<td>FSZ</td>
</tr>
<tr>
<td></td>
<td>8-10</td>
<td>PSZ</td>
</tr>
<tr>
<td>$Y_2O_3$</td>
<td>8</td>
<td>FSZ</td>
</tr>
<tr>
<td></td>
<td>2.8-3</td>
<td>PSZ</td>
</tr>
<tr>
<td>Yb$_2$O$_3$</td>
<td>10</td>
<td>FSZ</td>
</tr>
<tr>
<td>Sc$_2$O$_3$</td>
<td>11</td>
<td>FSZ</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>20</td>
<td>FSZ</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>PSZ</td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>15</td>
<td>PSZ</td>
</tr>
<tr>
<td>Ta$_2$O$_5$</td>
<td>15</td>
<td>PSZ</td>
</tr>
</tbody>
</table>
1.4.4 Mechanism of stabilization

The addition of oxide dopant ions (e.g. Ca$^{2+}$, Mg$^{2+}$, Y$^{3+}$) into ZrO$_2$ host lattice substitutes the Zr$^{4+}$ ion with the formation of oxygen vacancies to maintain the charge balance. The oxygen vacancies are distributed randomly in the lattice and are the main reason for the ionic conduction exhibited by stabilized zirconia. This process can be represented by the following defect equations [49]

$$\text{MO} + \text{Zr}^{2+}_n + \text{O}_n^X \rightarrow \text{M}_{2n}^+ + \text{V}_o^- + \text{ZrO}_2 \quad \text{(1)}$$

$$\text{M}_2\text{O}_3 + 2 \text{Zr}^{2+}_n + \text{O}_n^X \rightarrow 2\text{M}_{2n}^+ + \text{V}_o^- + 2\text{ZrO}_2 \quad \text{(2)}$$

Where MO = CaO, MgO, BaO…etc & M$_2$O$_3$ = Y$_2$O$_3$, Sc$_2$O$_3$, La$_2$O$_3$…etc

M$_{2n}^+$, M$_{2n}^+$ represent divalent and trivalent dopant ions substitution, respectively and V$_o^-$ represents oxygen anion vacancy.

Insertion of a dopant ion that differs in size to Zr$^{4+}$, perturbs the surrounding host lattice and Zr-O and dopant-O bond length decreases. The displacement of ions surrounding the dopant was investigated from the calculated and experimental interatomic separations for doped ZrO$_2$ and was found that oxygen ions adjacent to an oxygen vacancy are displaced towards it, as depicted in Figure 2, confirming that the dopants lead to considerable perturbation of the local structure of ZrO$_2$ lattice [49].

![Figure 2. Displacement of ions by incorporation of dopant in ZrO$_2$ host lattice [49]](image)
The formation of oxygen vacancies, to maintain the charge neutrality, lead to different dopant-vacancy cluster configurations. For example, an oxygen vacancy may be located at a nearest-neighbor (NN) or a next-nearest-neighbor (NNN) site to the dopant ion as shown in Figure 3.

![Diagram of dopant-vacancy clusters in doped ZrO$_2$ showing NN and NNN configurations](image)

**Figure 3.** Schematic diagram of dopant-vacancy clusters in doped ZrO$_2$ showing NN and NNN configurations [49]

The dopant–oxygen bond length in the NN case is smaller than the dopant–oxygen bond length for the NNN configuration. It was observed [49] that the larger dopants are more strongly bound to an oxygen vacancy at the NNN site, whereas the smaller trivalent metal ions generally favors the cluster with a NN vacancy. In general, metal dopants with a smaller radius than Zr$^{4+}$ (0.84 Å) prefer to be seven fold coordinated; on the other hand, the larger dopants, for example, Y$^{3+}$, prefer to be eight fold coordinated and therefore impose a cubic symmetry on the surrounding sub-lattice with enhances the concentration of oxygen vacancies. This may be one of the reasons why larger dopants like Y$^{3+}$ acts as good stabilizer of cubic phase.

Khan et al. [49] calculated the energy of various alkaline-earth and rare-earth doped-ZrO$_2$ systems using the simulation approach and found a strong correlation between the energies of these solid solutions with the dopant size. Among alkali earth dopants, Ca$^{2+}$ and Mg$^{2+}$ dopants showed minimum solid solution energy (Figure 4) and easily incorporated into zirconia host lattice. The simulation results were
consistent with experimental results for Ca$^{2+}$, which not only stabilized the cubic phase, but also improved ionic conduction. However, in case of Mg$^{2+}$, experimental

![Graph showing energy of alkaline-earth and rare-earth doped-ZrO$_2$ systems as a function of dopant size [49]](image)

results shown the instability of MgO-ZrO$_2$ solid solutions at high temperatures. The incorporation of Ba$^{2+}$ (ionic radius 1.36 Å) into ZrO$_2$ host lattice was highly unfavorable, probably due to the large ‘mismatch’ in ion size with the host Zr$^{4+}$ (0.84 Å). Among rare-earth dopants (Y$^{3+}$, La$^{3+}$, Nd$^{3+}$, Gd$^{3+}$), Y$^{3+}$ showed lowest (and negative) solid solution energy and the results were in well agreement with experimental work in which Y$_2$O$_3$-stabilized ZrO$_2$ is one of the most widely used solid electrolytes for applications requiring high oxygen ion conductivity. Gd$^{3+}$ has also a favorable energy and is widely use in CeO$_2$-based oxygen ion conductor [67].

1.5 Significance of nano-crystalline material

The nano-structured materials exhibit unique physical and chemical properties due to their limited size, high surface to volume ratio and a high density of corner or edge surface sites [68,69]. Two principal factors, i.e., (i) increased relative surface area and (ii) quantum effects result into significantly different properties of nano-
materials from bulk materials. Thus nanoparticles have a much greater surface area per unit mass compared with larger particles. It means that a given mass of material in nanoparticle will be much more reactive than the same mass of material made up of larger particles and the availability of active surface sites will be more resulting into enhanced reactivity. As the particle size decreases, the increasing number of surface and interface atoms generates stress/strain and concomitant change in structural properties. The presence of uncoordinated atoms (like corners or edges) or oxygen vacancies in an oxide nano-material produces specific geometrical arrangements. The quantum size significantly affects the electronic, electrical, mechanical, thermodynamic and magnetic properties of the material [68,69].

Therefore, nanostructured zirconia based ceramics are important because of their special mechanical and electrical properties than micro structured zirconia. These are tough, wear resistant and show a low thermal conductivity. One of the advantages of the nano size zirconia powder is its higher sinter activity as compared to its coarse grain counterpart, which results in a considerable decrease of sintering temperature [70]. A nano-crystalline zirconia owing to high surface-to-volume ratio is further expected to exhibit enhanced catalytic properties compared to microcrystalline zirconia.

1.6 Synthesis of nano-crystalline zirconia and stabilized zirconia

The properties of a nano-material are significantly influenced by the method used for its synthesis. The nanomaterial synthesized by different approaches may exhibit significantly different physical and chemical properties. The wet chemical methods with a ‘bottom-up’ approach, in which individual building blocks are assembled to a large molecule or polymerized into bulk material, are considered to be the promising methods for the production of high purity and chemically homogeneous
powders with excellent properties. A number of specific methods grouped in this approach have been commonly used to prepare nano-crystalline zirconia and stabilized zirconia and are briefly discussed as below:

1.6.1 Synthesis methods

1) Precipitation method

This method involves the solution of a salt precursor (chloride, nitrate, etc.) in water/alcohol/mixture to precipitate the oxo-hydroxide in presence of a base. Aqueous ammonia and urea are commonly used bases as precipitating agents. The addition of other metal salt precursor has usually been done by sequential or simultaneous (co-precipitation) addition during the preparation of doped or mixed metal oxides. This is an effective method in the preparation of powders with uniform composition on a nanostructure level with reproducible results. Nano-crystalline pure as well as doped-stabilized zirconia has been commonly prepared by this method [46, 60, 71-74].

2) Sol-gel method

This method prepares metal oxides via hydrolysis of precursors, usually alcoxides in alcoholic solution, resulting in the corresponding oxo-hydroxide sol. Condensation and polymerization of sol forms a network gel of the metal hydroxide which after appropriate drying and calcinations lead to ultrafine porous oxide gel. Sol-gel method has been widely used in the manufacture of ceramics due to its ease in controlling the purity, homogeneity, and physical characteristics at low temperature [75-77].

In sol–gel methods, the polymeric precursor route or Pechini-type in-situ polymerizable complex approach is also used [78,79]. The polymer precursor route avoids the segregation of metal ions throughout gel formation; the metal ions are coordinated by the chelating ligand and uniformly incorporated into the polymer
matrix via coordination bonds and intermolecular interactions of van der Waals and/or hydrogen bonding. The water-soluble polymers such as poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), poly(ethylenimine) (PEI) and poly(ethylene glycol) (PEG) are often used. Pechini-type sol–gel method involves metal nitrates, PEG and acetic/formic acid to construct the homogeneous polymer precursor solution on the molecular level via coordination bond and intermolecular interactions. The acid chelates the metal cations having a homogeneous distribution of cations through the polymeric chains. Formic acid seems more effective in preventing the metal hydroxides from segregation during the gel formation due to its stronger acidity and coordinating capability compared to acetic acid [78]. Generally, alkoxide have been employed as metal precursors, however non alkoxide or metal salt precursors have also been used in sol-gel method [80]. As non-silicate tetravalent alkoxides such as zirconium are very sensitive to moisture, inorganic acids, carboxylic acids, β-diketones or other complexing ligands are used as inhibitors/complexants/modifiers to control the reactivity and to decrease the hydrolysis rate of alkoxide precursors [81]. Nano-crystalline pure and stabilized zirconias have been prepared through different approaches of sol gel method [79-86].

3) Hydrothermal method

In this case, the reaction solution is heated thermally either in an inert atmosphere or using an autoclave with or without pressure. Stabilized zirconia has been prepared by hydrothermal treatment of amorphous co-precipitate to avoid the fast coarsening of primary particles and consequent formation of hard aggregates [87, 88].
4) **Gel combustion method**

Gel combustion routes are based on the gelling and subsequent combustion of a solution containing salts of the desired metals (usually nitrates) and some organic fuels, such as urea, carbo-hydrizide, citric acid glycine, etc. [89]. The combustion process is due to an exothermic redox reaction between nitrate ions and the fuel. The metal nitrate precursor decomposes in presence of fuel along with the formation of flammable gas such as NH₃, HNCO, O₂ and NO. After the solution reaches the point of spontaneous combustion, it begins to burn and becomes a solid which is burnt, at temperatures over 1000°C. The surface charge and particle dispersion of zirconia in aqueous suspension can be modified with the additions of different dispersants such as diester phosphate (PE) to reduce the agglomeration and thus the size of zirconia particles [65]. The whole process takes only a few minutes to yield zirconia powders; however, the combustion route forms the flammable gas, which is not environment friendly. Different stabilized zirconias have been prepared by this method [89-91].

5) **Template or micelles method**

This method involves the use of surfactant as a templating agent which is removed after the formation of the material resulting into the formation of porous structure. Various anionic, cationic or neutral surfactants have been used to prepare porous structure depending on the size of the surfactant. The surfactant helps to control the size by limiting the growth and agglomeration of particles. The surfactant can be added to the reaction media in any synthesis method mentioned above. Cetyltrimethylammonium bromide (CTAB) is the most commonly used cationic surfactant as the template to prepare mesoporous zirconia and stabilized zirconia [92]. Besides CTAB, other molecules of higher carbon chain such as octanoic acid (C₇H₁₅COOH) [93] and Pluronic surfactants (tri block copolymers of poly ethylene
and propylene oxide; \((PEO)_n(PPO)_m(PEO)_n\) [94] have also been used as a structure-directing agent to prepare mesoporous zirconia and stabilized zirconia.

Besides wet chemical methods, solid state mixing by ball milling of powder [95,96] and air plasma spraying [97] methods have also been used to prepare nano-stabilized zirconia.

1.6.2 Drying methods

After the preparation of the material by using any of the above mentioned methods, the drying of the material is an important step to remove physically adsorbed water/solvent, or trapped solvent inside the pores of gel/precipitate. The drying of the material significantly affects its textural properties. There are different methods of drying such as thermal, supercritical and freeze drying. The simple thermal drying is widely used; however during thermal drying the pores collapsed due to liquid-vapor interface formed inside the pores and thus reduced the surface area. The dried gel having sintered pores and lower surface area is called “xerogel”.

In order to avoid this problem, supercritical drying methods have been used and found appropriate way to remove solvent without changing texture of the pores [98]. The supercritical drying has been done at low temperature using some supercritical gases like CO$_2$ and at high temperature where solvent itself is used as supercritical fluid. At low temperature supercritical drying, the supercritical fluid is introduced in pores replacing the solvent and then the supercritical fluid is taken out from the pores without disturbing the texture of the pores. At high temperature supercritical drying, the supercritical condition is established to convert the solvent into supercritical fluid and then supercritical fluid is drained from pores without changing the texture of pores. The supercritical drying avoids the liquid-vapour interface inside the pores and the resulting fine, porous material having higher surface area is called “aerogel”.

Besides supercritical drying, freeze drying of the gel is done in freeze dryer; the gel is frozen by liquid nitrogen in the freeze drier to remove the solvent under vacuum [99] and the material is called as “cryogel”.

The drying method strongly influences the properties of a material and therefore a xerogel, aerogel and cryogel have significant variation in their structural and textural properties.

1.7 Characterization techniques

Characterization of the prepared material is an important study to evaluate its physicochemical properties and the catalytic activity using different instrumental techniques. The characterization of zirconia involves the analysis of structural, textural and morphological properties. The structural properties of zirconia are the identification and quantification of its crystalline phase, crystallinity, and crystallite size. The textural properties include the surface area, pore volume, pore size and pore size distribution. Besides these, the thermal analysis of zirconia provides important information for its crystallization. Scanning electron microscopy (SEM) shows the shape of zirconia material prepared by different methods. These characterization techniques are briefly discussed as below:

1.7.1 Structural properties

a) Powder X-ray diffraction study

The lattice planes in a crystal are designated as \((hkl)\) and characterized by Miller indices \(h, k\) and \(l\), which are reciprocals of the intersections between the lattice plane and the three crystallographic axes that span the unit cell of the crystal. The incident X-ray beam \((S_o)\) and the lattice planes have to be oriented in a certain angle \((\theta)\) to allow diffraction. Beams reflected at parallel lattice planes in the distance \((d_{hkl})\) interfere and give an intensity maximum, which occurs as peak in X-ray
diffractogram, if their path difference $2d_{hkl}$ is an integer of wavelength ($\lambda$). This condition has been described as Bragg’s law [100],

$$n \lambda = 2d_{hkl} \sin \theta$$

The X-ray diffractogram is the pattern obtained by plotting the intensity of the diffraction lines versus the angle $2\theta$. In powder samples with randomly oriented crystallites, the same amount of the crystallites has the right orientation for the diffraction for all lattice planes. If, instead, a certain pattern is preferred, the intensity of some reflections is lowered or increased. Information about the lattice parameters is available from peak position. The sharpness of the diffraction lines is determined from their intensity together with their breadth, which is called the full width at half maximum (FWHM). The breadth of the peak is increased with decreasing crystallite size. The XRD pattern of the sample shows the intensity of X-ray diffracted by different plane of the crystals at different angles.

The crystal phase identification is based on the comparison of the set of reflections of the specimen with that of pure reference phases or with database. The three crystalline phases of zirconia are identified by characteristic PXRD patterns as per PXRD data base files as shown in figure 5 [101].

The crystallinity (%) of the phases is calculated by comparing the areas of the characteristic peaks of the phases. The percent composition of each phase was calculated from the peak areas, $h\omega$, where $h$ and $\omega$ are the height and the half width of the X-ray diffraction pattern at the characteristic peaks [102].

$$\% \text{ Composition of phase A} = \frac{(hw) \text{ of phase A}}{100} \frac{1}{(hw) \text{ of phase A} + (hw) \text{ of phase B}}$$
X-ray diffraction line broadening analysis is used to determine crystallite size of the crystalline phase of zirconia using Scherrer formula [103]

Crystallite size = K. λ/ W. \( \cos \theta \);

Where, K = shape factor, λ = wavelength of X-ray radiation used, W = difference of broadened profile width of the experimental sample (W_b) and standard profile width of the reference sample (W_s), \( \theta \) = angle of diffraction.

**Figure 5.** PXRD Stick Pattern of crystalline phases of zirconia [101]
b) FT-IR study

FT-IR spectroscopic study leads to a great deal of information, e.g., the presence of various groups, structure, hydrogen bonding, etc. The interaction of IR radiation with molecule results in change in the dipole moment and vibrational energy level of the molecule. The activation of the molecule leads to different mode of vibrational motions such as stretching (symmetric and asymmetric) and bending and promotes the molecule in higher vibrational energy level. The energy of the stretching vibrational motion is higher than that of the bending vibration and the asymmetrical stretching motion is higher in energy than the symmetrical stretching motion. The transition in vibrational energy levels of the molecule gives IR spectrum, which is the graph between the wave number and the % transmittance or absorbance. The nature of bonding between oxygen and zirconia surface shows the bands between 400-700 cm\(^{-1}\).

1.7.2 Textural properties (N\(_2\) adsorption desorption isotherm study)

The determination of surface area, pore volume, pore size, pore size distribution, porosity and pore shape is an important requirement in material characterization. The area of a rough surface is called as external surface area and the area of the pore walls is an internal surface area. These properties are most often determined by using gas adsorption method (physisorption), which gives adsorption isotherm. The adsorption isotherm is the relationship between the amount of the gas adsorbed and the relative pressure at constant temperature. The samples are degassed under vacuum at 120 °C for 4 hours, prior to measurement, to evacuate the physisorbed moisture. Nitrogen (at 77 K) is generally used as most suitable adsorbate. Surface area is most often determined by BET-method (Brunauer-Emmett-Teller method) from physisorption isotherm data using BET equation [104].
Where $P/P_o = \text{relative pressure}$, \( n^a = \text{volume of gas adsorbed} \), \( n_m^a = \text{volume of gas adsorbed in monolayer formation} \), \( c = \text{constant} \), indicates the shape of isotherm and order of magnitude of the adsorbent-adsorbate interaction.

The first step in interpretation of a physisorption isotherm is to observe the shape of isotherm, which tells the qualitative nature of the surface coverage and the way of pore filling. IUPAC classification [104] has classified the isotherms in four types as shown in figure 6(a). Type I is reversible isotherm, showing steady adsorption after certain relative pressure ($P/P_o$). It is characteristic of microporous materials (pore size < 2 nm). Type II is also reversible isotherm and is showed by non-porous or macroporous materials (pore size > 50 nm). Isotherm shows unrestricted monolayer-multilayer adsorption upto high $P/P_o$. Type III isotherms are found in the systems, in which the overall adsorbent-adsorbate interactions are weak in comparison with relatively strong adsorbate-adsorbate interactions and shows unrestricted monolayer-multilayer adsorption. Type IV isotherm is completely different from others and is having a hysteresis loop and the plateau at high $P/P_o$. This type of isotherm is given by mesoporous materials. The first part of the isotherm shows monolayer formation and initial multilayer formation on the wall of mesopores. The knee of the isotherm represents the completion of monolayer and start of multilayer. However, at certain $P/P_o$, there is a sharp increase in adsorption, which shows the capillary condensation in mesopores. The pore volume is calculated by BJH- method (Barrett, Joyner and Halenda method) [104].

The hysteresis loops are informative tool to know the shape, size of mesopores and their distribution. IUPAC classification categorizes the hysteresis (Figure 6b) into
four groups [104]. Type H1 represents narrow distribution of relatively uniform mesopores. Type H2 shows complex pore structure. Type H3 and H4 show unlimited adsorption at high relative pressure, indicating the absence of well-defined mesopores. Type H3 hysteresis is obtained in layer structure, showing narrow slit shape pores.

![Figure 6. (a) Types of isotherms. (b) Types of hysteresis](image)

1.7.3 Thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are performed using simultaneous DSC/TGA to study the decomposition pattern and stepwise and total weight loss in the samples. Samples are scanned in given temperature range (50-1000 °C) with certain heating rate under flow of an inert gas (N₂).

1.8 Application of pure and stabilized zirconia

Zirconia is an important multi-functional transition metal oxide being widely used in variety of applications; few are listed below:
i) **Ceramic and Refractory:**

Pure cubic and stabilized zirconia is widely used as a refractory material, in insulation, abrasives, enamels and ceramic glazes. Tetragonal zirconia polycrystals (TZP) offers superior strength, toughness and wear resistance and thus is used in cutting tools, abrasion wheels etc. [44]. Zirconia is used to make ceramic knives. Because of its hardness, zirconia based cutlery stays sharp longer than a stainless steel equivalent. Stabilized zirconia is used as thermal barrier coating (TBC) due to its very low thermal conductivity in jet turbine and diesel engines to allow operation at higher temperatures. Another low thermal conductivity use is ceramic fiber insulation for crystal growth furnaces, fuel cell stack insulation and infrared heating systems.

ii) **Electro-ceramic:**

Fully/partially stabilized zirconia has the unique ability to allow oxygen ions to move freely through the crystal structure at high temperatures. The high ionic conductivity makes it one of the most useful electro-ceramics used for oxygen sensors in exhaust gases and solid oxide fuel cells (SOFC). YSZ is the most commonly used as the solid electrolyte in SOFC, which enables oxygen ion conduction while blocking electronic conduction, operated at high temperatures (800-1000 °C) [1].

iii) **Bio-ceramic:**

Partially stabilized zirconia has important biomedical applications, for example in dentistry in the manufacture of (i) sub frames for the construction of dental restorations such as crowns and bridges and (ii) strong, extremely durable dental prostheses constructed entirely from monolithic zirconia. It is also used as reinforcement material with hydroxyapatite in bone tissue formation. Tetragonal zirconia polycrystals (TZP) are most desirable bio-ceramic used in Arthroplasty due to high surface hardness and smoothness [45].
iv) **Catalyst:**

In recent years, zirconia has attracted much attention as a catalyst and catalyst support due to its unique amphoteric character and redox properties [6,21]. Its catalytic properties are especially promising because of its high thermal stability. It has been reported as a better catalyst and catalyst support compared to classical materials such as Al\(_2\)O\(_3\), SiO\(_2\) and TiO\(_2\). The catalytic activity of ZrO\(_2\) as a single oxide is attributed to the bi-functional acid-base properties, the oxidizing and reducing properties and the terminal and bridged surface OH groups. After modification with certain anions such as SO\(_4^{2-}\), it acidity has found to increase higher than that of H\(_2\)SO\(_4\) and therefore it is recognized as a superacid [24]. The modified zirconia, viz. sulfated ZrO\(_2\), zirconia substituted mixed oxides such as Ce\(_x\)Zr\(_{1-x}\)O\(_2\) solid solutions, and various transition metal stabilized zirconia have been reported to be effective for several organic reactions, combustion and gas phase reactions. For example, isomerization of alkane [7], alkene [8], epoxides [9] and aromatics [10], dehydration of alcohols [11] and decomposition of nitrous oxide [12]. It also works as a photocatalyst [22, 23]. The catalytic performance of zirconia depends on the structural and textural properties, which are in turn affected by the synthesis method adopted and calcination temperatures. Besides catalysts, it is also used as a catalyst support resulting higher activity and selectivity for many reactions. Various reactions such as hydrogenation of olefins, benzene, carbon mono- and dioxide, Fischer-Tropsch synthesis, hydrogen production from steam reforming of methanol and ammonia decomposition, low-temperature water-gas shift reaction, and hydro-desulfurization have been reported over zirconia-supported catalysts with higher rates and selectivity than with other supports [12-20]. Zirconia having high surface area, meso-macro porosity and high thermal stability has attracted the attention of material chemistry in
recent years [105]. Shaped zirconias are making an impact on advanced catalyst formulation by modifying surface area, porosity, acidity and basicity. Because of their relatively low toxicity, the vast majority of zirconium compounds are classified as non-hazardous to the ecosphere, a real asset in the light of environmental concerns [106].

v) Optical:

Zirconia is an interesting material for optical applications. It is a good white pigment and a good opacifier. It has been used as a coating for titania white pigments in organic paint binders [4]. Zirconia has low vibration energy resulting much higher efficiencies of luminescence in zirconia matrix, which makes its potential use as a host for telecommunication amplifier and cathode radiation tubes [107]. Zirconia is a direct band gap insulator and high-k dielectric material and has applications as an insulator in transistors.

In recent years, substantial efforts have been focused on the fabrication of composites of ceramic materials and rare-earth oxides. One of the reasons for this effort is the combination of the optical properties of rare-earth ions and the unique qualities of ceramic materials. Among these ceramic materials, zirconia is a potential choice due to its superior properties such as optical transparency, chemical stability, high thermal expansion coefficient, low thermal conductivity, etc. [54]. The ability to stabilize its crystalline phase at ambient temperature further provides an opportunity for correlating the optical properties of rare-earth ions with its crystalline structure. Different rare-earth ions doped zirconia material may achieve different optical properties and may be useful as potential luminescent materials with application in optoelectronics and nanoscopic optical storage elements such as in electroluminescent flat panel display, color plasma panel display, fluorescent lamps, cathode ray tubes
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and compact disk (CD) readheads etc. [108-111]. Historically zirconia was used for glowing rods in Nernst lamps.

vi) Gem:

Single crystals of the fully stabilized cubic zirconia are commonly used as a substitute for diamond in jewellery due to its close visual likeness to diamond; having a cubic crystal structure and a high index of refraction like diamond. To distinguish a good quality cubic zirconia gem from a diamond is difficult visually; the jewellers distinguish by a thermal conductivity tester to identify cubic zirconia by its low thermal conductivity (diamond is a very good thermal conductor). Because of its low cost, and durability cubic zirconia is the most gemologically and economically important competitor for diamonds since its commercial production from 1976.

In view of the above mentioned diverse applications of zirconia, we have prepared zirconia [112] by sol-gel and conventional precipitation method followed by thermal and supercritical techniques and studied the structural (crystalline phase and crystallite size) properties of zirconia. We obtained interesting results and thus extended the studies in the present thesis, wherein we have studied the effect of synthetic and drying techniques on structural, textural and morphological properties of pure as well as doped zirconia.

1.9 Summary of work in present thesis

The present thesis consists of eight chapters having below discussed contents.

The first chapter of the thesis deals with the literature survey of zirconia, history, structure, stabilized zirconia, effect of various dopants and their concentration on structural stabilization of zirconia, the various methods to synthesize the zirconia
and stabilized zirconia, characterization techniques and various applications of pure and stabilized zirconia.

**The second chapter** deals with the synthesis and characterization of nanocrystalline zirconia prepared by sol-gel (SG) and conventional precipitation (PP) method. The effect of thermal drying of zirconia gel in an oven and under vacuum has been studied. The samples were characterized by Powder X-Ray Diffraction (PXRD), FT-IR Spectroscopy, Thermo-gravimetric (TG) and Differential thermal (DT) analysis, N$_2$ adsorption-desorption isotherm and Scanning Electron Microscopy (SEM). The crystallite size, crystalline phase, phase transformation and textural properties of zirconia samples prepared by both techniques are determined and compared with a special emphasis on the stabilization of nano-crystalline tetragonal phase and its transformation into nano-crystalline monoclinic zirconia.

**The third chapter** extends the synthesis and characterization of nanocrystalline zirconia aerogels prepared by sol-gel technique followed by supercritical drying (SCD) using $n$-propanol under supercritical temperature (235°C) and pressure (51 bar) and compared with zirconia xerogel samples prepared by conventional thermal drying method as described in chapter 2. The effect of various parameters such as supercritical temperature, zirconia precursor and its concentration, and pH of gel on the structural and textural properties of zirconia aerogels have also been studied.

**The fourth chapter** describes the synthesis and characterization of nanocrystalline CaO and MgO doped zirconia by precipitation and sol-gel methods. The effect of synthesis method, dopants (CaO and MgO) and their concentration (8 and 16 mol%) on formation and stabilization of cubic crystalline phase and also on crystallite size of zirconia in the temperature range of 500-900°C has been studied.
The fifth chapter describes the synthesis and characterization of nano-crystalline Y$_2$O$_3$ doped stabilized zirconia prepared by various methods such as sol–gel, co-precipitation, CTAB surfactant and ultrasonication techniques. The effect of drying method such as conventional drying, supercritical and microwave drying was also studied. The crystallinity, stabilization of cubic crystalline phases was studied at different calcination temperature in the range of 500 to 1200° C.

The sixth chapter describes the catalytic applications of Y$_2$O$_3$ doped stabilized zirconia as a solid catalyst for liquid phase epoxidation of styrene with molecular O$_2$ in the presence of DMF as solvent. This chapter is divided into two parts:

In chapter 6(I) a series of non-sulfated and sulfated Y$_2$O$_3$ doped stabilized zirconia catalysts with Fe and Co co-cations was prepared, characterized and studied for above said reaction. Effect of various reactions parameters such as temperature, time, amount of DMF, absence of DMF solvent and presence of water have been studied to optimize the reaction parameters. The re-usability of the catalysts has also been studied.

Chapter 6(II) deals with microwave-assisted epoxidation of styrene with molecular O$_2$ over sulfated Co–Y–ZrO$_2$ solid catalyst, which was found to yield maximum conversion of styrene and selectivity of styrene oxide studied in chapter 6(I) with a view to enhance the conversion/selectivity and compared with conventional thermal heating studied in chapter 6(I). The effect of temperature, time, microwave irradiation (400, 800W) and various solvents on the conversion and selectivity has been studied.

The seventh chapter of the thesis discusses about the synthesis and characterization of rare earth (Eu, Dy and Er; 1mole %) doped-ZrO$_2$ and doped- Y$_2$O$_3$ stabilized ZrO$_2$ (YSZ) and their optical properties. The optical properties of the
samples were measured by Diffuse Reflectance Spectroscopy (DRS) and Photo-luminescence (PL) spectroscopy.

The eighth chapter of the thesis comprises summary and conclusions of the work done for the synthesis and characterization of zirconia prepared by various synthetic and drying methods, addition of CaO, MgO and Y₂O₃ to prepare stabilized ZrO₂, application of Y₂O₃ doped zirconia as a solid catalyst for styrene epoxidation with molecular O₂, synthesis and characterization of rare earth (Eu, Dy and Er) doped zirconia and doped Yttria-Zirconia to study their optical properties, were summarized and plausible conclusions were drawn.

1.10 References

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http://en.wikipedia.org/wiki/Baddeleyite
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