CHAPTER 1

INTRODUCTION

1.1 NANOCERAMICS

Nanomaterials are defined as those materials whose length scale lies within the nanometric range, i.e. from one to a hundred nanometers. Within this length scale, the properties of matter are considerably different from the individual atoms, molecules and bulk materials. The physical, chemical, electrical and optical properties of these materials are size and shape dependent and they often exhibit important differences from the bulk properties. These unique properties are related to the large number of surface or interface atoms. Nanostructured ceramic materials have good refractory properties, good chemical resistance, good mechanical resistance and hardness both at normal and high temperatures; they are especially amenable to sintering and reactions with different oxides. The materials at nano scale have attracted many researchers in various fields from material science to biotechnology and genetics.
The interest for nanostructured ceramic materials which are synthesized in dimensions smaller than 100 nm has been growing in the last decades. The interest has been stimulated by the large variety of applications in industries such as fabrication of dense ceramics, sensors, batteries, capacitors, corrosion-resistant coatings, thermal barrier coatings, solid electrolytes for fuel cells, catalysts, cosmetics, health, automotive, bioengineering, optoelectronics, computers, and electronics etc. Currently, the importance of nanomaterials in the field of luminescence has increased, especially, as they exhibit enhanced optical, electronic and structural properties. Many new physical and chemical methods of preparations have also been developed in the last two decades. Nanoparticles and nanorods of several ceramic materials have been produced. More recent studies have revealed that optical, luminescence and other properties get modified by its shape and size, incorporation of impurity at different site and also due to the presence or absence of certain defects (Yatsui et al. 2002, Qu et al. 2002, Fox et al. 1988).

1.2 SOLID ION-CONDUCTING CERAMICS

There are two major groups of solid ion conducting material namely fluorite structured and perovskite structured materials. The three most common solid oxide electrolyte materials are doped ceria (CeO₂), doped zirconia (ZrO₂) (both are oxygen ion conductors) and doped barium zirconate (BaZrO₃) (a proton conductor). The concentration and type (ionic radius) of the dopants influence the material properties strongly. Dopants that cause the least strain and hence the least influence on the potential energy landscape of the parent lattice have the biggest effect on the conductivity.
In an oxide ion conductor, current flows by the movement of oxide ions through the crystal lattice. This is a thermally activated process, where the ions hop from one lattice site to the other (from one potential valley to the other) in a random way. When an electric field is applied, there is a drift in one direction superimposed on the random thermal motion. Ionic conduction depends on the mobility of the ions and therefore on temperature. At high temperatures, the conductivity can reach 1 S cm\(^{-1}\), which is of the same order of magnitude as for liquid electrolytes. For possible ionic conduction, the crystal must contain unoccupied sites equivalent to the occupied sites by oxygen ions in the lattice. The energy barrier must be small (\(\leq 1\) eV) for migration from an occupied site to an unoccupied site. This might seem strange since the relative size of the oxygen ions is large and it is therefore more likely that the smaller metal ions migrate in an electric field. In order to account to this logic, specifically there are only a few special structures that make oxygen ion migration possible. They are the fluorite structured oxides and perovskites.

1.2.1 Fluorite Structured Oxides

The cubic fluorite structured oxides are the most familiar and classical oxygen ion conducting materials. The crystal structure consists of a cubic oxygen lattice with alternate body centers occupied by eight coordinated cations. The cations are arranged into a face centered cubic structure with the anions occupying the tetrahedral sites. This leaves a rather open structure with large octahedral interstitial void. The general formula has the form MO\(_2\), where M is generally a large tetravalent cation, e.g. Zr, Ce. As Zr\(^{4+}\) is too small to sustain the fluorite structure at low temperatures, it has to be partly
substituted with a larger cation, called dopant. Doping involves usually substituting lower valence cations into the lattice. In order to maintain charge neutrality oxygen vacancies are introduced thereby allowing oxygen ion migration. An interesting feature of the fluorite structure is that it can sustain a high degree of substitution. As a result of high degree of substitution, a highly disordered material is formed which promotes ionic conduction. By substituting the host cation sites with either rare earth or an alkaline earth element, just as with yttria stabilized zirconia (YSZ), an increase of ionic conduction can be achieved.

Figure 1.1 Crystal structure of Yttria incorporated zirconia
Zirconia (zirconium dioxide, ZrO$_2$) in its pure form has a high melting temperature and a low thermal conductivity. The applications of pure zirconia are restricted because it shows polymorphism. It is monoclinic at room temperature and changes to the denser tetragonal phase from ~1000 °C. This involves a large change in the volume and causes extensive cracking. Hence zirconia has a low thermal shock resistivity. The addition of some oxides results in stabilizing the cubic phase and the creation of oxygen vacancy.

Partially stabilized zirconia (PSZ) is a mixture of a cubic and a metastable tetragonal ZrO$_2$ phase. Mixture of zirconia polymorphs results due to addition of insufficient amount of stabilizer. PSZ is also called tetragonal zirconia polycrystal (TZP). PSZ is a transformation-toughened material since the induced microcracks and stress fields absorb energy. PSZ is commonly used for making crucibles (refractory application) because it has a low thermal conductivity and a high melting temperature. The addition of 16 mol% CaO or 16 mol% MgO or 8 mol% Y$_2$O$_3$ (8YSZ) is needed to prepare fully stabilized zirconia (FSZ). The structure of the fully stabilized zirconia is cubic which

Figure 1.2 Mechanism of ion conduction in YSZ
does not undergo any further phase transformation when heated from room temperature up to 2500 °C. Because of its high oxide ion conductivity, YSZ is often used for oxygen sensing and solid oxide fuel cell electrolyte. Generally, it might be expected that an increase of the dopant concentration would lead to an increase of conductivity. But actually it holds good only in low dopant concentrations because at higher levels, the first and second electron coordination shells dopants start interacting with the oxygen vacancies and the conductivity decreases drastically.

Currently in fuel cells, the electrolyte of choice is zirconia stabilized by either 3 mol% Y₂O₃ (3YSZ) or 8 mol% Y₂O₃ (8YSZ). Despite the economic preparation process and remarkably lower electronic conductivity of YSZ it is not considered as the best solid ion conductor. Although, there are many other oxygen ion conducting materials, YSZ is considered as the most suitable material at present because of its abundance, chemical stability, non-toxicity and economic synthesis process. The world demand for YSZ is rising, but fortunately Zr is one of the most common elements of the earth’s crust usually in the form of silicate zircon (ZrSiO₄). This material has to be purified since SiO₂ tends to block the ionic and electron paths.

Yttria is the main stabilizer used and about 13-16 wt% have to be added to give a fully stabilized cubic material. Another interesting fluorite structured material is CeO₂ doped with 10 mol% Gd (GDC). It is especially useful for lower temperature applications. But GDC is an electron conductor in the reducing environment at the anode and hence short-circuiting is a major problem.
1.2.2 Perovskite Structured Oxides

The second interesting group of solid state ion conductors is the perovskites. The general perovskite stoichiometry is ABO$_3$. Due to the high stability of the structure and the wide variety of cations that can be accommodated within, perovskites have a wide range of properties which are suitable not only for SOFC but also as ferroelectrics, oxidation catalysts and superconductors. High ionic conductivity in perovskites is achieved by doping the material with trivalent elements such as Y on the Zr site of BaZrO$_3$ so that oxygen vacancies are introduced. The conductivity of ABO$_3$ perovskites strongly depends on the size of the ‘A’ and size of the ‘B’ cation, since the oxides have to migrate through a triangular space, consisting of two large ‘A’ cations and one smaller ‘B’ cation. The enlargement of this triangular space facilitates the migration of oxide ions through the lattice. Hence higher ion conductivity is expected with larger lattice dimensions.

Figure 1.3 Crystal structure of trivalent ion doped Barium zirconate and path for proton conduction
In order to incorporate hydroxyl groups into the vacant oxide sites, the material is exposed to humid atmospheres. The second proton of the water molecule attaches to some other oxygen atom in the structure. Due to the loose bonding between the hydrogen ion and the oxygen atom, conduction occurs easily by hydrogen ions jumping from one oxygen to the other. The perovskite BaZrO$_3$ have proved to be highly attractive since their structure is very tolerant and can accommodate large concentrations of dopants but less than in YSZ. Hence the ionic conductivity of perovskites is always less than that of YSZ.

1.3 TECHNICAL CHALLENGES IN USING CERAMIC SOLID ION CONDUCTING MATERIALS AS ELECTROLYTE IN SOFC

The traditional oxygen ion conductors that are familiar over 100 years and employed in solid oxide fuel cells (SOFCs) (Nernst 1899, Baur 1937) have met critical challenges due to the electrolyte material which is claimed as the heart of the SOFC. The conventional SOFC electrolyte material namely yttrium stabilized zirconia has an ionic conductivity of 0.1 Scm$^{-1}$ at high temperature ca. 1000°C. Such high temperature hinders the SOFC technology from commercialization. Many efforts have been focused on thin-film technologies on YSZ inorder to reduce the operating temperature (Shao and Sossina 2004, Huang 2007). However a thin film electrolyte cannot assure a long SOFC life as its operation involves mass transport processes which can affect the electrolyte property in one or another aspect thereby causing serious degradation. Moreover, the thin film YSZ also requires the operational temperature above 700°C. Discovery and development of materials that function at low temperatures are therefore a critical technical challenge.
Obviously, by reviewing typical SOFC electrolyte materials and the ionic conduction theory and analyzing the disadvantages in single-phase materials, the need for the development and theory of new materials can be ascertained.

Ceramic electrolytes are polycrystalline and consist of grains, grain boundaries, pores, etc. The grain boundaries often have a predominant role in significantly influencing the material’s ionic conductivity. Grain boundaries are interior contacts between particles which act as a barrier preventing the ionic conductivity. Ionic transport is blocked as the grain boundary conductivity is much lower than that of the grain. Therefore, the grain boundary engineering is the foremost factor to improve the ionic conductivity of the ceramic material. A clear idea of grain boundary performance in ceramic materials is important to control and optimize their properties. In the majority of oxygen ion conductors, the smaller the grain size, the higher the resistivity because of the inter-grain neck and contact. Moreover, the space charge effects tend to lower oxygen vacancy concentration near the grain boundaries.

1.4 ADVANCED NANOSTRUCTURED SOLID STATE IONIC CONDUCTORS

The study of nanostructured materials that can be used as solid-state ionic conductor named as ‘nanoionics’ is one of the important areas of research related to nanomaterials (Maier 2005). Nanoionics gained attraction in recent years due to its advanced energy conversion and storage applications (Arico et al. 2005). Nanoionics is also a key aspect in SOFC technology
According to Zhu (2009), the nano- and composite technologies can take in the concept of super-ionic conduction and manipulation of the interphases of the nanocomposites can overcome SOFC challenges thereby enhancing and improving material conductivity at significantly lower temperatures in the range 300–600°C. State of the art of the nanotechnology remarks a great potential for SOFC.

The recent developments are being carried out by widely using nanotechnology and nano-size materials for the conventional SOFC electrolytes with new supportive scientific principles. These most recent studies from nano-aspects have shown the common facts that the nanostructured ceria-based materials (Bellino 2006, Kim and Maier 2002, Ruiz-Trejo 2007) and YSZ (Garcia-Barriocanal 2008) exhibited strong conductivity enhancement, due to significantly larger area of grain-boundary or interface in nanostructured systems, which increases the concentration of mobile defects in the space-charge zone (Arico et al. 2005, Maier 2005). The effect of grain boundary limiting the ionic conductivity as discussed earlier in this section regarding bulk ceramic material changes at the nano-level with introduction of different functionalities and principles. The grain-boundary in ionic conduction suddenly turns from negative effect in the micron-sized materials to positive effect as an efficient promoter in the nano-sized materials. The development of advanced materials with different functionalities in the nanometric scale thus needs a very different approach, principle and theory. Nano-structured materials can enhance the conductivity due to strong grain-boundaries effects. A simple schematic representation of the ionic migration as proposed by Zhu (2009) with respect to size of the particle is shown in Figure 1.4. The mechanism of ionic migration is different at micrometeric and
nanometeric levels. At nanometeric level, the grain boundaries act as side paths for ion passage.

**Figure 1.4 Scheme of ionic migration at micrometer and nanometer levels**

Based on the fast ionic conduction or super-ionic conduction theory, the ionic conduction mechanism of advanced ionic conducting materials can be understood. The nanostructure must be such that it can offer long-distance channels or networks for ionic conduction/transport. In the two- or multiphase nanocomposite materials the co-existence of two-phase creates the interfaces and particle surfaces between the constituent phases, where the super-ionic conduction takes place. In nanostructures, the energy to form defects on the surfaces or interfaces is significantly lower than that inside the bulk structure. Therefore in such cases, even low temperature can activate sufficient ion mobility.

The disorder in structure is associated with high concentration of mobile ions in the interface as there is no bulk structural limit to create mobile ions. The interfaces have the capacity to contain high concentration of mobile
ions. The strong enhancement in conductivity is due to the fact that the transport channels/networks (from particle to particle at nanometer level) are long range in the interfaces than those of the bulk. In contrast, the effect occurs within a crystal unit cell at Angstrom level of the bulk.

Advanced multifunctional nanocomposites for low temperature SOFC are based on developing and modifying the physical, chemical and surface properties of nanoparticles to obtain new desired properties differing from the bulk counter-part materials. It is well known that the surface effect becomes more significant as the particle sizes decreases. At nano-level, the atoms are mostly concentrated on the particle surfaces in contrast to the bulk. It is obvious that these atoms lack coordination due to very high surface energy. Therefore they interact voluntarily with other material’s atoms as in the case of stabilization of one material by doping with another material. Such surface atoms or ions are highly mobile which results in super-ionic conduction at interfaces. Still better understanding of physics behind the ionic conductivity mechanism is obvious for the development of complex architectures of nanocomposites (shape and size). The super-ionic conductivity at low temperature is possible in two-phase nanocomposites with new architecture in which the interfaces act as ion highways resulting in super-ionic conduction in network with continuous paths. This has been dealt with by a theoretical approach reported by Zhu et al. (2008). The ion transport mechanism in interfaces is currently under study and needs extensive research both experimentally and theoretically. At present there is a lack of knowledge and theory on this particular area. Several concepts of the advanced material architectures are described based on the concepts of nanoscience.
1.4.1 Nanocomposites

Nanocomposites are formed by adding a secondary phase as inclusion into the parent material. This type of inclusion hinders the grain growth of nanostructures effectively. Nanocomposite may be formed as a nano-core particle with a nano-layer-shell formed by the second phase or by interaction between the constituent phases. In core-shell structure, the material components (i.e.) the core and shell/layer have different functionalities. These nano-functional particles commonly hinder energetic growth at high temperatures and prevent high activity in extreme atmospheres. Moreover they render new characteristics at interfaces between the two constituent phases. The nano-sized particle in single-phase materials possesses large surface area but the stability decreases due to high surface energy in the active and chemically uncontrolled conditions. In two-phase materials, the second phase particles can make the interfaces and surfaces with effective functions by maintaining stability through modified surface properties. Therefore the main concept is to choose a suitable second phase that enables effective interaction between particles and phases by altering the surface properties. Wang et al. (2008) have demonstrated a similar concept in which the core-shelled structures have exhibited a great thermal stability compared to single-phase material. The high surface energy and diffusion rate of the nanostructured composite materials and effective suppression of the grain growth at high temperatures by the presence of second phase makes it to be possibly considered as a new advanced functional material for SOFC application.
1.4.2 One-dimensional (1D) nanostructures

One-dimensional (1D) nanostructures (nanorods/nanowires) have attracted much interest for both scientific research and technological applications due to their unique physical and chemical properties (Xia et al. 2003, Lee et al. 2003). The 1D nanostructures are believed to have a longer continuous interface thereby revealing a higher ionic conductivity compared to nanoparticles (3D nanomaterials) based on the interface conduction theory. Therefore, application of 1D nanostructure in SOFC field will certainly gear up the material research directed toward this scope.

The 1D nanostructures have to be optimized and better aligned to achieve super-ionic conductivity. It is indeed a very probable electrolyte material as one dimensional nanostructure is supposed to have longer continuous conductive path at interfaces in nano-electrolyte which signifies higher ionic conductivity compared to the 3D nanoparticles. It is therefore considered as a new interesting subject for further concrete research.

1.5 SCOPE OF THE RESEARCH WORK

In this present research work, focus is directed on the ceramic nanomaterials and nanocomposites that find application as electrolyte material in Solid Oxide Fuel Cells (SOFC). For advanced ceramic components, the starting powder is of critical importance for optimization of the properties. It is now well recognized that the mechanical, electrical, chemical as well as
catalytic properties of the material can be improved by using nanopowders instead of conventional micron-sized powders. Particles on a nanoscale, with dimensions ranging from 1 to 100nm in at least one direction are of particular interest.

Nanocrystalline ceramic oxides show astonishing properties suitable for numerous applications and have opened attractive horizons for advanced materials development. Reducing the particle size to nanoscale of the precursor powder for SOFC components is advantageous. Using nanopowders as precursors for the manufacture of SOFC components have been demonstrated by Kim et al. (2007) and Lee et al. (2010) to enhance the performance of fuel cells operations. Sintering of nano-grained particles may occur at lower temperatures (Gil et al. 2011, German 1996, Vasylkiv et al. 2001) which is advantageous for both the electrolyte and the electrode-supported configurations. Besides processing considerations, lowering the sintering temperature decreases the grain size of the particles. Smaller grain size is claimed to lead to the formation of narrower grain boundaries. There are clues that narrower grain boundaries result in higher ionic conductivity. (Tikkanen et al. 2011). High density of defects in nano-structured materials provides a large number of active sites for ionic conduction and high diffusivity through nanometer-sized interphase boundaries to promote fast kinetics and ion transportation. Hence research in material science has become vital for developing better starting nanopowders for fabrication of SOFCs components. The ability to manipulate and engineer material synthesis and processes at atomic and molecular level can create radical new architectures, materials and structures with unique functionalities and characteristics.