

# ASSORTED PERSPECTIVES ASSOCIATED WITH NANO CERAMIC MATERIAL AND NANO COMPOSITE

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## ABSTRACT

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.

*Keywords: Nanoceramic, Nano Composite, Nano Material*

## INTRODUCTION

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).

### **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 ( $\text{CeO}_2$ ), doped zirconia ( $\text{ZrO}_2$ ) (both are oxygen ion conductors) and doped barium zirconate ( $\text{BaZrO}_3$ ) (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  $1 \text{ S cm}^{-1}$ , 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 ( $\sim 1 \text{ eV}$ ) 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.

### **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  $\text{MO}_2$ , 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.

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  $\sim 1000$  °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%  $Y_2O_3$  (8YSZ) is needed to prepare fully stabilized zirconia (FSZ). The structure of the fully stabilized zirconia is cubic which 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%  $Y_2O_3$  (3YSZ) or 8 mol%  $Y_2O_3$  (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 ( $ZrSiO_4$ ). This material has to be purified since  $SiO_2$  tends to block the ionic and electron paths. Ytria 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  $CeO_2$  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.

#### **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. 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.

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  $0.1 \text{ Scm}^{-1}$  at high temperature ca.  $1000^\circ\text{C}$ . Such high temperature hinders the SOFC technology from commercialization. Many efforts have been focused on thinfilm technologies on YSZ in order 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  $700^\circ\text{C}$ . 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.

#### **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.

### **CONCLUDING POINTS**

nanoceramics is a type of nanoparticle that is composed of ceramics, which are generally classified as inorganic, heat-resistant, nonmetallic solids made of both metallic and nonmetallic compounds. The material offers unique properties. Macroscale ceramics are brittle and rigid and break upon impact. However, nanoceramics take on a larger variety of functions, including dielectric,

ferroelectric, piezoelectric, pyroelectric, ferromagnetic, magnetoresistive, superconductive and electro-optical. Nanoceramics were discovered in the early 1980s. They were formed using a process called sol-gel which mixes nanoparticles within a solution and gel to form the nanoparticle. Later methods involved sintering (pressure and heat). The material is so small that it has basically no flaws. Larger scale materials have flaws that render them brittle. In 2014 researchers announced a laser process involving polymers and ceramic particles to form a nanotruss. This structure was able to recover its original form after repeated crushing. 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.

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