

DURABILITY AND INTEGRITY OF NANOCERAMIC BASED IMPLEMENTATIONS IN ASSORTED DOMAINS

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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. Nanoceramic 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.

Keywords: Ceramics, Nanoceramics, Nanoparticles

Introduction

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 lasering process involving polymers and ceramic particles to form a nanotruss. This structure was able to recover its original form after repeated crushing.

Over the past decade, nanoceramics have received significant attention as candidate materials due to their capability to demonstrate improved and unique properties in comparison with conventional bulk ceramic materials. Nanoceramics exhibit unique processing, mechanical, and surface characteristics such as superplasticity, machinability, strength, toughness, and bioactivity due to the fine grain size, abundant grain boundaries, and controllable crystallinity. This issue compiles five exciting manuscripts, which address recent trends and development in nanoceramics.

The optical properties of nanoceramics are addressed in three manuscripts. Optical nonlinear performance of silicon nanoparticles at different doping concentrations has been investigated by L. Chen et al. Their results show silicon nanoparticles generated by femtosecond laser ablation exhibit better saturable absorption performance at higher doping concentrations. Their results reveal the possibility to tune the optical nonlinearity of silicon

nanoparticles by changing the doping concentration.

In recent times, there are great interests in luminescent materials for efficient frequency conversion from infrared to visible radiation; oxyfluoride glass ceramics are ambivalent materials which can exhibit optical properties of fluoride single-crystals when they are doped with rare-earth ions. M. H. Imanieh et al.'s manuscript focuses on improvement of Er^{3+} emissions in two series of oxyfluoride glass ceramics ($\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Al}_2\text{O}$) containing CaF_2 nanocrystals doped with a fixed amount of Er^{3+} and Yb^{3+} through the heat treatment at different temperatures. They showed in their study that increasing the temperature of the heat treatment leads to a rise in the red and green emissions in the upconversion luminescence of the treated samples. Also, increasing the heat treatment temperature leads to the incorporation of Er^{3+} ions into CaF_2 crystals and can increase the Yb^{3+} concentration. Increased Yb^{3+} concentration improves the energy transfer and back transfer process between Er^{3+} and Yb^{3+} ions and as a result upconversion intensity can be increased.

Polymers have attracted a lot of attention as excellent host materials for encapsulation of metal nanoparticles like silver, gold, copper, and so forth. Many reports in the literature show attempts for synthesis of metal-polymer nanocomposites based on polymers, with the possibility of variation in their optical, mechanical, and electrical properties for the application in photovoltaic and biomedical devices fabrication. M. Ghanipour et al. investigated the effect of silver nanoparticles doped in PVA on the structural and optical properties of composite films. Their results show that by embedding silver nanoparticles inside the polymer, a number of Bragg's planes in the structure of polymer and its crystallinity are increased noticeably. Ag-O bonds are formed in the films and the bandgap energy, refractive index, and dielectric constant of samples are decreased by increasing the concentrations of silver nanoparticles.

Two of the manuscripts deal with fabrication methods for high performance nanoceramics and nanomaterials; Q. Liu et al. reported the new method for fabrication of highly ordered Ti-Nb-Zr-O nanotube arrays through pulse anodic oxidation

of Ti-Nb-Zr alloy in monosodium phosphate containing 0.5 wt% HF electrolytes. The effect of anodization parameters and Zr content on the microstructure and composition of Ti-Nb-Zr-O nanotubes have been studied using experimental analysis and it has been found that length of the Ti-Nb-Zr-O nanotubes increased with increase of Zr contents.

Y. Qiang et al. investigated the materials and chemical properties of BCFN dense ceramic membrane with submicron-CYDC porous layer by the partial oxidation of coke oven gas (COG) in hydrogen production. The results of their study show that this structure exhibits higher stability and no chemical reaction at high temperature environment. Also, the influences of YDC modification on the surface kinetics and oxygen permeation rates of BCFN membranes have been analyzed.

By compiling these papers, we hope to enrich our readers and researchers with respect to synthesis, characterization, and applications of nanoceramics.

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).

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.

Properties

Nanoceramics have unique properties because of their size and molecular structure. These properties are often shown in terms of various electrical and magnetic physics phenomena which include:

- Dielectric - An electrical insulator that can be polarized (having electrons aligned so that there is a negative and positive side of the compound) by an electric field to shorten the distance of electron transfer in an electric current
- Ferroelectric - Dielectric materials that polarize in more than one direction (the negative and positive sides can be flipped via an electric field)
- Piezoelectric - Materials that accumulate an electrical charge under mechanical stress
- Pyroelectric - Material that can produce a temporary voltage given a temperature change
- Ferromagnetic - Materials that can sustain a magnetic field after magnetization

- Magnetoresistive - Materials that change electrical resistance under an external magnetic field
- Superconductive - Materials that exhibit zero electric resistance when cooled to a critical temperature
- Electro-optical - Materials that change optical properties under an electric field

Nanotruss

Nanoceramic is more than 85% air and is very light, strong, flexible and durable. The fractal nanotruss is a nanostructure architecture made of alumina, or aluminum oxide. Its maximum compression is about 1 micron from a thickness of 50 nanometers. After its compression, it can revert to its original shape without any structural damage.

Synthesis

Sol-gel

One process for making nanoceramics varies is the sol-gel process, also known as chemical solution deposition. This involves a chemical solution, or the sol, made of nanoparticles in liquid phase and a precursor, usually a gel or polymer, made of molecules immersed in a solvent. The sol and gel are mixed to produce an oxide material which are generally a type of ceramic. The excess products (a liquid solvent) are evaporated. The particles desired are then heated in a process called densification to produce a solid product. This method could also be applied to produce a nanocomposite by heating the gel on a thin film to form a nanoceramic layer on top of the film.

Two-photon lithography

This process uses a laser technique called two-photon lithography to etch out a polymer into a three-dimensional structure. The laser hardens the spots that it touches and leaves the rest unhardened. The unhardened material is then dissolved to produce a "shell". The shell is then coated with ceramic, metals, metallic glass, etc. In the finished state, the nanotruss of ceramic can be flattened and revert to its original state.

Sintering

In another approach sintering was used to consolidate nanoceramic powders using high temperatures. This resulted in a rough material that

damages the properties of ceramics and requires more time to obtain an end product. This technique also limits the possible final geometries. Microwave sintering was developed to overcome such problems. Radiation is produced from a magnetron, which produces electromagnetic waves to vibrate and heat the powder. This method allows for heat to be instantly transferred across the entire volume of material instead of from the outside in.

The nanopowder is placed in an insulation box composed of low insulation boards to allow the microwaves to pass through it. The box increases temperature to aid absorption. Inside the boxes are susceptors that absorb microwaves at room temperature to initialize the sintering process. The microwave heats the susceptors to about 600 °C, sufficient to trigger the nanoceramics to absorb the microwaves.

History

In the early 1980s, the first nanoparticles, specifically nanoceramics were formed, using sol-gel. This process was replaced by sintering in the early 2000s and then by microwave sintering. None of these techniques proved suitable for large scale production.

In 2002, researchers tried to reverse engineer the microstructure of seashells to strengthen ceramics. They discovered that seashells' durability come from their "microarchitecture". Research began to focus on how ceramics could employ such an architecture.

In 2012 researchers replicated the sea sponge's structure using ceramics and the nanoarchitecture called nanotruss. As of 2015 the largest result is a 1mm cube. The lattice structure compresses up to 85% of its original thickness and can recover to its original form. These lattices are stabilized into triangles with cross-members for structural integrity and flexibility.

Nanoceramic is a unique dielectric material – a powerful electrical insulator that is also a good conductor of heat. The thermal properties of Nanoceramic make it ideal for use as an electrical barrier in thermally demanding applications, particularly LED applications such LED packaging, UV LED applications for curing printer inks and LED modules.

Nanoceramic is usually manufactured into large sheets similar to metal clad PCBs (MCPCBs) or insulated metal substrates (IMS) for the PCB market or smaller tiles with thin film circuitisation for the semiconductor market. It is also possible to convert the surface of complex 3D shapes to a Nanoceramic, enabling “Chip on Heat Sink” applications or use very thin aluminium foil to create a flexible substrate.

The Nanoceramic layer is made up of tiny crystals of alumina – a material which, although it is a powerful electrical insulator, has a good thermal conductivity. This makes it an ideal dielectric – providing it can be applied densely and uniformly. This is the secret of Nanotherm's patented electrochemical oxidation (ECO) process.

This nano-crystalline structure has a grain size of 20–40nm. These grains are atomically bonded to the surface of the aluminium, and are packed very densely across the surface – forming an electrically impervious barrier. With such a fine crystal structure, the material retains aluminium's natural flexibility – giving an ability to create flexible thermally conductive substrates on thin aluminium foils, but also high resistance to temperature cycling.

Finally, the dielectric material is fully inorganic. Unlike epoxy or polymer dielectrics, a Nanotherm dielectric can withstand high temperatures – it is unlikely that the ceramic will fail below the aluminium backplate's melting point

Table 1: Compositions and Dimensions

Composition:	Nano-crystalline aluminium oxide (alumina, Al ₂ O ₃)
Crystalline grain size:	20-40nm
Thermal conductivity:	6-7.2 W/mK R _{th} = 0.02 °C.cm ² /W
Layer thickness:	3-30 µm
Temperature resistance:	> 500 °C (limited by melting point of aluminium)

Conclusion

Nanoceramics are usually manufactured from nanoscale powders using forming and sintering techniques. As nanopowders are harder to compact due to intense internal friction, their compaction often involves methods including impulse and

hydrostatic forming, slip and gel casting and fluid extrusion. One of the key challenges in manufacturing nanoceramics is usually the intensive growth of grain during sintering in normal conditions. Two basic methods are used to prevent this effect: addition to the base powder (blend) of insoluble doping agents that are localised at the boundary of grains and prevent their coalescence, and the application of special methods and modes of compaction and sintering of ceramic materials that make it possible to significantly decrease the duration and/or temperature of high-heat manufacturing stages (impulse pressing, hot pressing, some types of presintering). All of these methods are described in more detail in the term entry "sintering of nanoceramics". The structure-sensitive properties of nanoceramic materials may differ to a great extent from the properties of conventional ceramics with micron-size grain. Certain mechanical (Al_2O_3), electric (Y:ZrO_2) or optical ($\text{Nd:Y}_2\text{O}_3$) properties may improve, but the nature of property changes depending on the size of grain is extremely subjective and is conditional on both the physical nature of a subject property and the physical-chemical features of the ceramics. Medical technology used nanoceramics for bone repair. It has been suggested for areas including energy supply and storage, communication, transportation systems, construction and medical technology. Their electrical properties may allow energy to be transferred efficiencies approaching 100%. Nanotrusses may be eventually applicable for building materials, replacing concrete or steel.

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