APPLICATIONS OF ADVANCED CERAMICS IN SCIENCE, TECHNOLOGY, AND MEDICINE

Editors:
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Frontiers in Ceramic Science

(*Volume 3*)

Applications of Advanced
Ceramics in Science, Technology, and Medicine

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Applications of Advanced Ceramics in Science, Technology, and Medicine

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PREFACE

Advanced ceramics are specified as the new class of ceramic materials made up of high purity synthetic chemicals. In recent years these ceramics gained much research attention in various applications due to their excellent performance. These advanced ceramics are composed of oxides, carbides and nitrides. Ceramic composites which include both the combinations of oxides and non-oxides Ceramic materials are the different class of materials composed of non-metallic stable and inorganic materials. They are brittle, electrically insulated and thermally insulated materials prepared with combination of more than single element. The ceramic materials will have distinct properties due to their grain boundaries in the materials undergo misalignments with nearby grains and their variations in the structure and quality in the perfections and contributions along with shape and size and material internal stress which they are exposed. For the few decades' people have observed the tremendous increase in the properties like ferroelectric, ferromagnetic, pyroelectric, dielectric and magnetoresistance, superconducting and gas sensing applications. These ceramic materials also became main materials for the advanced technologies like energy transformation storage and supply and also in the manufacturing, medical field technology and transportation, information technology *etc*. Hence, awareness and knowledge about ceramics and their derived nanomaterials with conceptual understanding are important for the advanced material community.

Advanced Ceramics and Applications in Science, Technology and Medicine explores the various advanced ceramic materials and their down to earth applications in distinct fields such as actuators, energy storage, environmental, 3D printing, electronics, biomedical and EMI shielding. This book provides an overview of the structural and fundamental properties, synthesis strategies and versatile applications of advanced ceramic materials and their composites. This book will be beneficial for students, research scholars, faculty members, R & D specialists working in the area of material science, solid-state science, chemical engineering, power sources and renewable energy storage fields and nanotechnologists. Based on thematic topics, the book contains the following 12 chapters:

Chapter 1 discuss briefly about the importance of piezoelectric actuators and also the principle of piezoelectric actuators. Besides, it is outlined on various advanced ceramic materials for the applications in piezoelectric actuators. In addition to this, some actuator operating methods like finite element method, topology optimization method *etc*. are also discussed.

Chapter 2 presents briefly an introduction of ceramics, different types of ceramic materials and role of ceramic materials in the evaluation of supercapacitors. Further, it is focused on different advanced ceramic electrode materials for supercapacitor applications. In addition to this some fabrication techniques like hydrothermal technique, molten salt technique, solution precursor flame spray *etc*. is discussed as well.

Chapter 3 focused on future perspective of magnetocaloric effect in refrigeration process and the isothermal entropy and adiabatic variation are the main properties to confine the refrigeration process. Also, the magnetic materials such as Mn doped Fe alloys and rare earth elements such as Gd, La, Ce *etc*. mixed composites and their properties are discussed.

Chapter 4 discusses the efficiency of the thermoelectric power generation depends on the figure of merit of the materials and also on the low thermal conductivity and high electrical conductivity. Several ceramic materials and their applications in the field of power generation are also discussed.

Chapter 5 reviews different ceramic materials including their electromagnetic parameters. The electromagnetic absorption property of the ceramic composites and pure ferrites are discussed. Furthermore, the applications of the advanced ceramics in defense systems, microwave communications and biomedical fields are summarized.

Chapter 6 briefly presents the discussion on the effect of electromagnetic radiation on the electronic goods, human health and defense system was elaborated. Furthermore, various ceramic materials were introduced for reducing the electromagnetic radiation pollution thereby microwave absorption process. It is focused on the parameters like magnetic loss and dielectric loss for each ceramic material. Subsequently, the applications of microwave absorbers in various fields were elucidated.

Chapter 7 concentrates on electromagnetic wave interference mechanism and the effected parameters to find the strength of shielding. Also discusses the derived material such as ferrites and its composites, carbon-based materials for shielding the EM interference. In addition, ferrite and polymer composites especially conducting polymer composites have been discussed.

Chapter 8 discusses the presence of intrinsic polarizations into the ferroelectric materials helps them to get polarized easily on the application of the electric field. Also, the mechanism and applications of ferroelectric materials ($Bi_{3.25}La_{0.75}Ti_3O_{12}$, Barium hafnium titanate, $La_3Ni_2NbO_9$ *etc*.) in different fields like ferroelectric memory devices, electro caloric devices, magneto electric devices, DRAM capacitors *etc*. have been discussed.

Chapter 9 reviews the transport properties of semiconducting glasses along with amorphous properties of various materials. In addition, some of the synthesis techniques such as thermal evaporation, chemical vapour deposition, melt quenching *etc*. have also been discussed.

Chapter 10 presents the applications of 3D printing ceramic materials in various fields. Also discusses the advantages of 3D printing over conventional techniques.

Chapter 11 focused on bio ceramics and preparation of bio ceramics by advanced 3D printing technology. Besides, different inorganic materials used to print bio ceramics such as alumina, zirconia, Leucite, lithium disilicate and mica-based ceramics for different applications in dentistry and orthopedics are also discussed.

Chapter 12 presents briefly the origin of ceramics, its advantages and the historical back ground of the ceramic materials and the classification of ceramics. Moreover, antimicrobial activity and the antimicrobial applications of advanced ceramics are summarized.

KEY FEATURES

- Overviews on advanced ceramic materials and their derived composites.
- Coverage on basic research and application approaches.
- Addresses a wide range of applications in actuators/sensors, energy conversion and storage, 3D printing, antimicrobial, EMI shielding and microwave absorbers.
- Explores challenges and future directions of advanced ceramic materials.

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CHAPTER 1

Advanced Ceramics for Piezoelectric Actuators

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Abstract: Nowadays, researchers concentrated on the advancements of new types of precision actuators to satisfy the increasing demand for high precision positioning technology. Owing to fast response, high precision, and compact structure, the piezoelectric actuators attracted much attention. In the advancement of science and technology, the ceramics play a vital role. In this chapter, we mainly focussed on applications of piezoelectric actuators in different fields such as nano metrology, and industries. Even, the different advanced ceramics for piezoelectric actuators were discussed.

Keywords: Acoustic actuators, Dielectric properties, Piezoelectric effect.

1.1. INTRODUCTION

In many areas such as MEMS, NEMS, nano metrology and biological engineering, the demand for ultra precision and nano plating technologies have been increased along with the development of science and engineering [1 - 3]. Accordingly, the significance of nano positioning systems has been increased in many industrial and research areas [4, 5]. The conventional actuators like DC-motors, AC-motors, hydraulic motors, *etc*., can fulfill the above requirements in the large scale positioning systems. However, the resolution of those actuators is not high [6 - 8]. Besides, the electromagnetic interference affects the performance of the conventional electromagnetic motors; no electromagnetic resonance can be generated by the piezoelectric actuators and even cannot be affected by electromagnetic interference. Therefore, in recent years, the researchers have

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focussed on introducing new kinds of actuators to meet the demands of nano-positioning systems. In this connection, piezoelectric actuators gained much attention owing to their quick response, simple structure, self-locking, *etc*. In addition, these actuators exhibit the resolution in nanoscale and suitable for nano positioning systems. Till now these piezo actuators are used in numerous fields such as optical lens systems [9, 10], aerospace [11, 12], and atomic force microscopy [13, 14], *etc*. In general, the piezoelectric materials which can be utilized as actuators are also called piezoelectric ceramics which consist of a specific crystal structure [15, 16]. They exhibit some unusual properties which make them special when compared to others. Those properties are due to a direct piezoelectric effect and indirect piezoelectric effect. In the case of the direct piezoelectric effect, these materials generate an electric charge by subjecting with mechanical stress. Similarly, in the inverse piezoelectric effect, the stain is developed in the same material by the application of the electric field. The direct effect is used in piezoelectric sensors while the inverse effect is used in actuators [17, 18]. In this chapter, we focussed on the inverse effect of piezoelectric ceramics and their applications in actuators.

1.2. ADVANCED MATERIALS FOR PIEZOELECTRIC ACTUATORS

In continuation with the development of designing the new type of piezoelectric actuators, Markus Flossel *et al*. [19], introduced a new module design based on the LTCC (Low-Temperature Co-fired Ceramic)/PZT (Lead Zirconate Titanate) multilayer ceramics for the actuator applications. This new technology involves the lamination of PZT ceramic plate sintering with the green layer LTCC followed by sintering to attain a sensor or actuator segment. (Fig. **1.1**) of the reference [19], represents the design of LTCC/PZT. Further, they reported that the functioning of the designed module is estimated by measuring dielectric properties and recording the hysteresis loops. In addition, they measured the deflection and reported that at a resonance frequency of 19.7 Hz, the prepared ceramic module exhibits the maximum deflection of 130 x 10^{-6} m which is in static mode, whereas in dynamic mode the same module shows the deflection of 550 x 10^{-6} m. Furthermore, through the metal die casting technique, the prepared modules are combined with Al (aluminium) matrix for further enhancement of the properties of the designed module. However, this new technology combines the microsystem technology of LTCC and piezoelectric technology of PZT which allows great improvement in practical applications such as electronic control, sensing and actuation.

Table 1.1. Advanced ceramic materials for piezoelectric actuator applications.

S.No.	Material	Synthesis Method	d_{33} (CN^{-1})	Electro Strain (in %)	Applications	Ref.
1	LTCC (Low-Temperature Cofired Ceramic)/PZT (Lead Zirconate Titanate) multilayer ceramics				Actuator, sensor, electronic control	[19]
2	$0.91K_{1/2}Bi_{1/2}TiO_3$–0.09 ($0.82BiFeO_3$-$0.15NdFeO_3$-$0.03Nd_{2/3}TiO_3$ ceramics	conventional solid-state and mixed route		0.16	actuator	[20]
3	$(Na_{0.48-x}K_{0.48-x}Li_{0.04})Nb_{0.89-x}Ta_{0.05}Sb_{0.06}O_3$-$xSrTiO_3$ ceramics	tape casting method and solid-state reaction method	650		audible sound device applications	[21]
4	$Pb(Mn_{1/3}Nb_{2/3})$ $0.07(Ni_{1/3}Nb_{2/3})$ $0.10(Zr_{0.5}Ti_{0.5})0.83O_3$ ceramics	conventional mixed oxide synthesis technique	386		piezoelectric speakers	[23]
5	$Ba_{1-x}Ln_{2x/3}Zr_{0.3}Ti_{0.7}O_3$ ceramics	solid state reaction technique		0.087	energy storage and actuator applications	[25]
6	periodically orthogonal poled method to barium titanate based ceramics			0.36	large actuation at low temperature and low frequency	[27]
7	$(Zr_{0.49}Ti_{0.51})_{0.94}Mn_{0.014}Sb_{0.02}W_{0.014}Ni_{0.02}O_3$ ceramics	calcination technique	278		micromechatronic devices	[28]
8	Li-doped BNT ($Bi_{0.5}Na_{0.5}TiO_3$) ceramic materials	solid state reaction technique	600		actuator applications	[30]

Amir Khesro *et al*. [20], synthesized lead-free ($0.91K_{1/2}$ $Bi_{1/2}TiO_3$-0.09 ($0.82BiFeO_3$-$0.15NdFeO_3$-$0.03Nd_{2/3}TiO_3$) ceramics for actuator applications with good thermal stability and fatigue resistant. These samples were prepared through conventional solid-state and mixed routes. The outcomes revealed that the prepared ceramics exhibit high electro strain of 0.16% at 6000 V/mm with a 10% variation from room temperature to 448 K. Therefore, the ceramics show good stability in this temperature range. Also, they designed a multilayer actuator through cobalt firing with Pt internal electrodes. These multilayer actuators exhibit thermal stability up to 300°C with a small variation of 15%. Further, the same ceramics show high fatigue resistance with both multi and mono layers. Hence, these advanced ceramics show the superior properties and are potential candidates for actuators when compared to all other lead-free ceramics. The following Table **1.1** represents some of the advanced ceramic materials used for

CHAPTER 2

Advanced Ceramics for Supercapacitors

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Abstract: In recent years, research is going on to introduce new types of electrode materials to satisfy the increasing demands for efficient energy storage devices. Among various energy storage devices, the supercapacitors gained a lot of attention owing to their long cyclic life, environment-friendly nature and high-power density. In this view, global research has been reported to this rapid development of fundamental and applied aspects of supercapacitors. In this chapter, we have given a brief description of different ceramic electrode materials along with their fabrication techniques for supercapacitor applications.

Keywords: Energy Density, Hydrothermal Technique, Molten Salt, Solution Precursor Flame Spray, Specific Capacitance, Supercapacitors.

2.1. INTRODUCTION

Etymologically, the term ceramic has been invented from two Greek words "keramos", which means "Potter's clay and "keramikos" means "clay products". Ceramic material is a "refractory, inorganic and non-metallic material which is often crystalline" or "the material which is formed by the use of heat". The advances in manufacturing techniques and the challenges posed by new applications led to the development of advanced ceramics. The capability of operating at temperatures greater than metals makes the ceramics a potential candidate for many structural applications like engine components, valves, bearings, *etc*. Ceramics having a low coefficient of thermal expansion and high thermal conductivity find applications in the field of electronics like capacitors,

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superconductors, magnets and transducers. Modern engineered ceramics are known for their advantages like more strength, high operating temperatures, improved toughness, high resistance to melting, bending, stretching, corrosion, heat, physical stability, hardness, chemical inertness, biocompatibility, superior electrical properties, suitability in mass production and tailorable properties makes them one of the most versatile materials. When decreased density and larger melting points are required to enhance the efficiency and speed of the process, advanced ceramics are taking the place of metals.

2.2. ADVANCED CERAMICS

The bond between ceramic particles differentiates the advanced/engineering ceramics from conventional ones. In advanced ceramics, the particles are combined at grain-boundaries by means of similar energy equilibrium mechanism, whereas in conventional ceramics, particles are bonded by a weak interlocking or mechanical linking, because the impurities that are present will restrict the self-bonding of the particles. Based on their mechanism, the advanced ceramics are classified as metal oxide ceramics, glass ceramics, carbides and nitrides.

2.2.1. Metal Oxide Ceramics

Some of the metals are also used as the main constituent of ceramics called metal oxide ceramics. Alumina, beryllia and zirconia are examples of metal oxide ceramics which are used in advanced ceramics in their pure form. The features of the above said ceramics are discussed below.

Salient Features of Alumina

- It can be mixed with chromium/oxides of silicon/magnesium/calcium and can be used at 3500ºF as long as they are not subjected to thermal shock and highly corrosive atmospheres.
- In general, alumina strength decreases beyond 3700ºF.
- Up to 1500ºF, they have good creep resistance.
- They are vulnerable to corrosion from steam, sodium and strong acids.

Salient Features of Beryllia

- Ceramic materials made up of Beryllia are expensive and excellent heat dissipators and electrical insulators as well.
- Possess extremely good thermal shock resistance, low coefficient of thermal expansion and high thermal conductivity.

Salient Features of Zirconia

- Of all ceramics, Zirconia is having the highest melting point which is about 4000^{o}F.
- Strongest and toughest ceramics are made from transformation-toughened zirconia ceramics like zirconia strengthened alumina (ZTA), Y-TZP (yttria stabilized tetragonal zirconia polycrtystals) *etc*.
- Further, Y-TZP ceramics are used in pump and controller mechanisms where corrosion and wear resistance are required.
- ZTA ceramics possess low density, improved thermal shock resistance and economical than Y-TZP. These ceramics are used in transportation equipment.

2.2.2. Glass Ceramics

These types of ceramics are obtained from molten glass. On subjecting to heat, this molten glass will be crystallized. These ceramics find applications in cooking utensils, table ware, smoothe cooktops *etc*. By controlling the crystalline structure in the host glass matrix, properties can be altered. Lithium-aluminium-silicate (LAS or beta beta spondumene), magnetism-aluminium-silicate (MAS) and alumina-silicate (AS) are the mostly used glass ceramics because at higher temperatures, these three ceramics are stable, possess near-zero coefficients of thermal expansion and also oppose oxidation.

Salient Features of LAS

- No appreciable thermal expansion up to 800^{o}C.
- Low thermal expansion due to high silica content.
- Strength also decreases due to silica.
- Attacked by sulfur and sodium.

Salient Features of MAS

- Stronger and corrosion resistant.
- MAS when mixed with aluminum titanate exhibits good corrosion resistance upto 2000^{o}F.

Salient Features of AS

- Obtained by discharging lithium out of lithium aluminum silicate particles.
- It is corrosion resistant and strong.
- Utilized in turbine engines.

Another ceramic which is as stronger as alumina is machinable glass ceramic technically called as Macor. It possesses various electrical and high temperature

CHAPTER 3

Advanced Ceramics for Magnetocaloric Effect in Refrigerators

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Abstract: In this chapter, we have reviewed the advanced ceramics which are used for the refrigeration or cooling process. The refrigeration process is carried out using the magnetocaloric effect, *i.e.*, the variation of specific heat and thermal energy as a function of temperature and magnetic field. The ceramics of magnetite and rare earth alloys of magnetic composites are briefly discussed.

Keywords: Ceramics, Ferrites, MCE, Refrigeration.

3.1. INTRODUCTION

The magnetic refrigeration derived from the magnetocaloric effect played a vital role in viewing the environment-friendly technology. From the last decade, the research in the direction of the magnetocaloric based materials and their characterization techniques were improved proportionally. The major cause of the existing this technology is its terrific alternative technology rather than the used gas compression or expansion-based refrigeration technology. In this, a magnetic solid is used as the refrigerator agent rather than the sources of greenhouse effect in the refrigerator [1 - 5]. In the commonly used refrigeration process, the fluids such as isobutene, carbon dioxide have been used as a solution. This makes flammability and hence the researchers get interest in this field. The use of ceramic materials in refrigeration cooling technology has resulted in research. Magneto-caloric materials are the part of the magneto-ceramic material offering application for cooling at room temperature in the place of hazardous and traditional gas refrigerators. Mainly, in the last few decades, some of the theore-

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tical studies show rod like magnetic materials which maximize a refrigeration device capacity [6]. In addition to this, the ceramic material possesses the improved mechanical and chemical stability with the organic and inorganic metals and polymers [7]. The magnetocaloric effect (MCE) is defined as the temperature changes from maximum to minimum and then it reaches to minimum upon application of external magnetic field on the magnetic material. It was theoretically explained by Warburg in 1881, later many of researchers continued studies on this effect, in 1949 the scientist Giauque gets Noble Prize in Chemistry as obtaining MCE effectively.

Generally, the MCE is a magneto-thermal phenomenon which is connected to coupling between lattice and external magnetic field. The MCE can be formulated based on the magnetic domain entropy (D_{SM}) and changes with temperature (Dt_{ad}) adiabatically, if the magnetic ceramics exposed to the external varying magnetic field [8]. The MCE is an aspect of some magnetic materials when the external magnetic field applied. Then, the heat up variation is taken place. Furthermore, the alignment of the atomic magnetic dipoles depends on the direction of the applied field and they become cool-down, once the applied field is removed. The material which exhibits this effect is named as MCMs (magnetocaloric materials). The materials can be characterized through the way of measuring temperature variation upon application of external magnetic field. The main parameters for the calculating MCE are the isothermal entropy variation Δs_{iso} and adiabatic temperature ΔT_{ad} of magneto caloric materials below external magnetic field variation at adiabatic conditions. The experiments are carried out through direct and indirect measurements to get MCE properties to obtaining AMR modeling and adiabatic temperature variation [9 - 11]. The direct method is temperature dependent technique in which the MCM is exposed to external field. Precisely, one can attain the adiabatic temperature change, whereas the second one depends on the magnetization and heat capacity measurements. In the indirect method, by studying the magnetizing curves which were obtained at temperature and applied field through isothermal procedure. Based on the thermodynamic model and first principle models, we can approach to evaluate adiabatic temperature variation of the system [12]. In particular, the thermodynamic model is commonly utilized in magnetic refrigeration to estimate the MCE in mathematical models of AMR-cycles [13 - 16]. By using the state of equations, we can identify the relation among the applied magnetic field, temperature and magnetization. However, the Weiss mean field theory (MFT) is commonly used as thermodynamic model for the evaluation of the magnetocaloric effect. Also, the MFT was applied to calculate the total entropy of the ferromagnetic material using the temperature variation with respect to external magnetic field [17]. Although in the first-principle models, it is found on an estimation of the interchange magnetic moments and coupling energies of magnetocaloric materials.

3.2. MAGNETOCALORIC MATERIALS

In following section, some of the crystalline materials are considered which the parts of the magnetocaloric materials. Recently, the magnetocaloric materials are mainly synthesized using the rare earth (RE) elements. Also, they define the parameters of MCE in rare earth free systems. Further, in the year 2000, Gschneidner & Pecharsky [10] studied the magnetocaloric nature of pure lanthanide elements. Nevertheless, one must indicate that in certain RE metals, there exists the robust improvement of MCE for small changes in field over ultrafine layers when their thickness is under the helix-period. Then, no magnetic order is formed, wherein the Ho-ultrathin film, the magnetocaloric curves demonstrated the shape like caret for traditional ferromagnetic materials [18, 19]. The Curie temperature of T_C=121 K, and T_{ad} was improved as a function of magnitude in regard to bulk samples (T_{ad} =1.3 K and 0.08 K for H =0.2 T for thin film and bulk samples, respectively) [20]. In the case of cubic phases (Fd3m space group), the rare earth atoms create a diamond unit cell while the remaining atoms are surrounded by the rare earth atoms establishing tetrahedral. In that lattice system, two magnetic sublattices come into view. They are: one is observed *via* magnetic rare earth atoms and other observed *via* traveling electron-magnetism owing to TMs. Herein, the $RECo_2$ composites, both magnetic sublattices are coupled for light RE-elements (for example Sm, Pr and Nd are ferro magnets) and coupled for anti-parallel weighty RE elements (for example Er, Ho, Gd, Dy and Tb are ferrimagnets).

Shen *et al*. [21], recently, reported a system of binary La-Fe phase-diagram which displays an immiscible-system; wherein no inter-metallic composites are developed. The mixing of minor quantity of Si/Al permits the development of ferromagnetic systems with FCC-$NaZn_{13}$-type structure comprising of 112 atoms per unit cells. These inter-metallic complexes show identical magnetic nature. Hu *et al*. [22], reported that for $LaFe_{11.4}Si_{1.6}$, Δs_{iso} is nearer to 20 $Jkg^{-1}K^{-1}$ at 210 $KJkg^{-1}$ for H=5T. It was attributed to a first-order traveling electron which encountered magnetic transition and the change in volume does not affect the crystal symmetry. The compositional effects caused to loss the travelling electron-metamagnetic transition and also lead to SOPT [29]. This even decreases the magnetocaloric effect and indicates the irrelevant loss of hysteresis.

The system of $Gd_5(Si, Ge)_4$ which shows the MCE and related to the RE5X4 family, encounters a magneto-structural first ordered phase evolution between orthorhombic Gd_5Si_4/Sm_5Ge_4 polymorphic structures. These structures are close to the Gd_5Si_4 and Gd_5Ge_4 binary compounds consisting of relative structures. Besides, the monoclinic-structures exist in Si content range of 0.2 - 0.4 in the

CHAPTER 4

Advanced Ceramics for Thermoelectric Power Generation

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Abstract: In the future, a lot of problems can be faced in energy management due to the heavy consumption of renewable and non-renewable energy sources. This is because of the ever-growing population and huge usage of electronic appliances in modern life. Therefore, people are looking into different fields to increase energy demand. In this chapter, the role of advanced ceramics and their applications of thermoelectric technology were discussed. Also, an attempt was made to study different advanced ceramic materials that are used for thermoelectric power generation in recent years.

Keywords: Applications, Thermal Conductivity, Thermal Efficiency, Seebeck effect, ZT.

4.1. INTRODUCTION

Advanced ceramics are specified as the new class of ceramic materials made up of high purity synthetic chemicals. These materials are focused on different industrial applications due to their high performance. In addition, they are composed of oxides, carbides and nitrides. Accordingly, the advanced ceramic materials based on their compositions are classified into two categories oxide or non-oxide ceramics.

• Oxide ceramics include binary oxides, aluminates, ferrites, titanites, niobates, zirconates, *etc*.

• Non-oxide ceramics cover carbides, nitrides, borides, carbon, *etc*.

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• Ceramic composites include both the combinations of oxides and non-oxides.

Ceramic materials are a different class of materials composed of non-metallic stable and inorganic materials. They are brittle, electrically and thermally insulated materials prepared with a combination of more than a single element. The mechanical strength of these materials can be increased by sintering process [1]. The ceramic materials will have distinct properties due to their grain boundaries in the materials. These grain boundaries undergo misalignments with nearby grains and their variations in the structure. These variations can be the quality in the perfections, contributions along with shape, size and internal stress to which they are exposed. For the last few decades, scientists have observed the tremendous increase in properties like ferroelectric, ferromagnetic, pyroelectric, dielectric and magnetoresistance, superconducting and gas sensing applications. The chemical and thermal properties of oxide and non-oxide ceramics were increased by the different manufacturing techniques. These ceramic materials also became the main materials for advanced technologies like energy transformation, storage, supply, in the manufacturing, medical field technology, transportation and information technology as shown in Fig. (**4.1**).

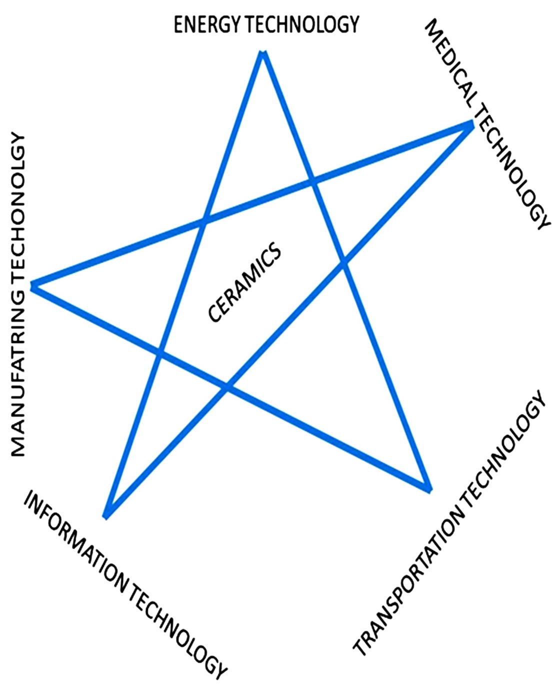

Fig. (4.1). Applications of advanced ceramics in various fields of technology.

4.2. ADVANCED CERAMICS AND THEIR PROPERTIES

4.2.1. Brittleness

The ceramic materials can sustain the brittleness up to a certain high temperature. This is happened because of the ceramic compounds containing the mixed ionic covalent bonds that dominant the division of atoms together. But they are brittle in nature at the room temperature.

4.2.2. Strength

Ceramic compounds, in general, will have very poor toughness; despite of increasing the toughness by adding the composites to a particular ceramic material. Ice-templating is a technique used to increase the mechanical strength of the ceramic material by subjecting it to the considerable mechanical loading. This maintains the microstructure of the ceramics and especially, the mechanical strength of the ceramic material. This property is very important for the applications like solid oxide fuel cells and water filtration.

4.2.3. Transparency

Due to large energy gap (E_g) values, few of the ceramic materials are transparent like glass optical fiber having the transparency of 96%. The ceramics which exhibit the transparency in nature cover the materials made up of sapphire, few valuable stones and optical fiber.

4.2.4. Chemical Insensitivity

The ceramic Pyrex glass is extensively used for preparation of bakeware and in chemical labs due to the high resistant nature of many destructive chemicals. In addition, these chemicals are of durable in nature at very large temperatures and are high resistant to the thermal shocks due to low coefficient of thermal expansion of value of about $33x10^{-7}$ K^{-1}.

4.2.5. Electrical and Thermal Influence

We know that diamond is a carbon material having highest thermal conductivity of the order of 1700 W/mK. Herein, the mechanism of the conduction is developed due to the phonons but not due to the electrons. In case of conductors, the valence electrons are free to move through the lattices, whereas in case of

CHAPTER 5

Advanced Ceramics for Microwave Absorber Applications

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Abstract: In the present world, electromagnetic radiation pollution has become a problematic issue in order to run electronic equipment as well. At this juncture, the necessity of absorbing the electromagnetic radiation emerged as a significant task. Thus, the advanced ceramic materials for microwave absorption property were developed. In the current chapter, the discussion on the effect of electromagnetic radiation on electronic goods, human health and defense system was elaborated. Furthermore, various ceramic materials were introduced for reducing the electromagnetic radiation pollution thereby microwave absorption process. Moreover, in order to evaluate the microwave absorption property of ceramics, we extracted the parameters like magnetic loss and dielectric loss for each ceramic material. Subsequently, the applications of microwave absorbers in various fields were elucidated.

Keywords: Dielectric loss, Magnetic loss, Magneto-ceramics, Microwave absorbers.

5.1. INTRODUCTION

It was observed that electromagnetic interference (EMI) or electromagnetic (EM) radiation pollution became a severe problem to the electronic goods, human body, military system and other living organisms [1 - 3]. In order to diminish the EMI, mechanisms like electromagnetic reflection, absorption and multiple reflections were developed. These mechanisms were observed consistently, in case of different pure ceramics (bulk & nano), ceramic composites, polymer composites and ceramic polymer composites. Within the three EMI removal mechanisms, the

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microwave absorption mechanism acquired good attention owing to the availability of more number of microwave absorbers materials. Normally, the microwave absorption efficiency depends on the absorption shielding efficiency (SE_A) and is given by $SE_A = 12.3t\ (\omega\sigma\mu_r)^{0.5}$, where ω = the angular frequency, t = the thickness of shielding material and μ_r = relative magnetic permeability [2]. The mathematical equation of SE_A indicated a fact that microwave absorption is dependent on electrical conductivity and magnetic permeability. That is, the microwave absorption property will be increased with an increase in electrical conductivity and magnetic permeability. However, it was a known fact that the electrical conductivity can be induced due to the high oscillating frequency of the spinning electric/magnetic dipoles. This high oscillating frequency of electric and magnetic dipoles can induce dielectric and magnetic loss parameters. Hence, it was confirmed that for achieving the efficient absorption of EM radiation, the absorber materials must show the high magnitude of the magnetic permeability, magnetic loss, dielectric constant and dielectric loss.

Apart from these electromagnetic parameters, the high abundance of physical and morphological parameters such as low density, porous structure and multiple polarization centers can enhance the microwave absorption property. The high magnitude of the above said parameters can give rise to the multiple reflection and scattering of microwaves thereby matching the impedance [1, 3]. From the vast literature survey, it was evidenced that the ceramic materials belong to the spinel ferrites, magnetic spinels, hexaferrites, magnetic perovskites, ceramic composites and ceramic polymer composites showed the high microwave absorption efficiency [2]. In view of this, the nickel zinc ferrites, nickel zinc cobalt ferrites, nickel cobalt zinc lanthanum ferrites, nickel zinc lanthanum ferrites, manganese zinc ferrites, barium zinc cobalt U-hexaferrites, barium hexaferrites, aluminium titanate and lanthanum iron oxide offered considerable microwave absorption behavior at giga hertz frequency range [2]. Once the microwave absorber materials are exposed to the EM radiation, the EM radiation enters into the interior of the material. Later on, the EM energy will be absorbed and converted into dissipated energy. Therefore, the electronic object will be prevented from EMI. A photograph of microwave absorber is provided in Fig. (**5.1**).

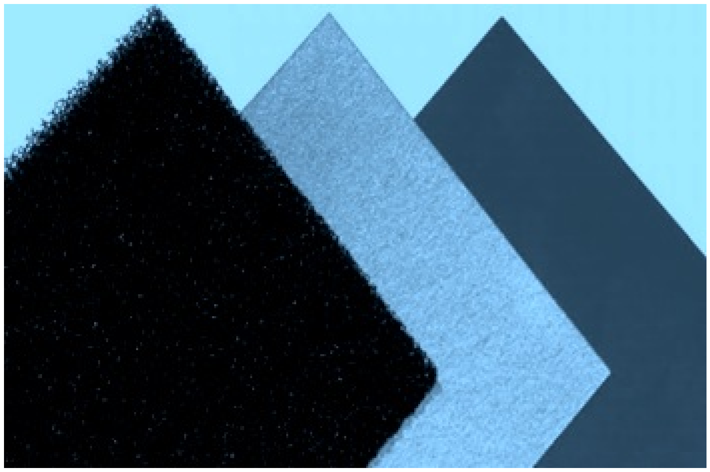

Fig. (5.1). Photograph of microwave absorber.

5.2. CERAMIC MATERIALS AND MICROWAVE ABSORBER PARAMETERS

In order to understand the microwave absorption property of ceramics and their composite materials, the electromagnetic parameters, absorption shielding efficiency and reflection loss were recorded in the Table **5.1**. It was seen that some magneto-ceramics and multiferroic ceramics offered high reflection loss (RL) and absorption efficiency (SE_A) at gigahertz frequency in their pure form. For example, the $Ni_{0.4}Co_{0.2}Zn_{0.4}Fe_2O_4$ [10]: -48.1 dB (1.1 GHz), $MnFe_2O_4$ [10]: -42.5 dB (9.4 GHz), $Co_{0.5}Mn_{0.5}Fe_2O_4$ [10]: -47.0 dB (10.5 GHz), $Ni_{0.4}Co_{0.6}BaTiFe_{10}O_{19}$ [10]: -46.9 dB (13.3 GHz), $Ni_{0.2}Co_{0.8}BaTiFe_{10}O_{19}$ [10]: -48.3 dB (16.0 GHz), $(MnNi)_{0.2}Co_{0.6}BaTiFe_{10}O_{19}$ [10]: -53.0 dB (13.5 GHz), $(MnNi)_{0.25}Co_{0.5}BaTiFe_{10}O_{19}$ [10]: -68.9 dB (14.1 GHz) and $La_{0.6}Sr_{0.4}MnO_3$ [10]: -40.9 dB (8.2 GHz) performed the high reflection loss at gigahertz frequency. Due to high RL value, the microwave absorption property of the above-mentioned ceramic material compositions was increased. Hence, we can use these pure materials as the electromagnetic shields/microwave absorbers. In addition to this, all these compositions showed high magnetic loss (at gigahertz) indicating the microwave absorption property. Moreover, the other electromagnetic parameters like dielectric constant, dielectric loss and magnetic permeability also revealed high magnitude of numerical values in support to the microwave absorption nature. On the other hand, the ceramic materials in alloys form like Fe/TiO_2 [10]: -45.1 dB (13.9 GHz), $Co_{1-x}S$ [10]: -45.8 dB (14.0 GHz), FeP [10]: -36.5 dB (15.1 GHz), Co_2P [10]: -23.3 dB (16.7 GHz), Fe/G [10]: -34.3 dB (17.1 GHz), NiCu [10]: -31.1 dB (14.2 GHz), Co_3Fe_7 [10]: -53.6 dB (14.2 GHz), FeSiAl [10]: -39.7 dB (1.4 GHz) and NdFe [10]: -55.9 dB (3.6 GHz) performed the high RL values

CHAPTER 6

Advanced Ceramics and Their Environmental Applications

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Abstract: Advanced ceramics are substances that are used for the preparation of ceramic materials with special properties. They are also called fine, engineering, high performance, high tech or technical ceramics. Traditionally, ceramics are known to be inorganic, non-metallic solids made of materials being powdered and then fabricated into material by applying heat which exhibit strength, hardness brittleness and low electrical conductivity. This chapter mainly deals with different types of advanced ceramics, their characteristics and their environmental applications.

Keywords: Environmental Applications, Technical Ceramics.

6.1. INTRODUCTION

Advanced or Technical ceramics come under the category of:

1. Material which is a combination of existing materials that undergo the process of modern approach in order to achieve surprising variations of regular properties that are exhibited by traditional ceramics.

2. Tough as well as electrically conductive ceramic products as some metals.

Processing of advanced ceramics and their development plays a significant role in going at a rapid pace. This is considered to be a revolution in terms of materials and the properties observed. Versailles project on advanced materials and standards (VAMAS) in 1993 has redefined the advanced ceramic as a non-metallic ceramic which is inorganic, which is a basic crystal of highly controlled

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composition, with detailed regulation and manufactured from raw materials that are highly refined and characterized to give specified and precise attributes [1].

An advanced ceramic has a number of distinguished features like:

1. Basically crystalline (without glassy component nature).

2. Exhibiting microstructures which are engineered to have the size and shape of a grain with porosity.

3. Having large phase distributions *i.e.* second phases such as fibres and whiskers are arranged, controlled and carefully planned. This process requires processing and composition with perfect regulation. Processing includes clean-room processing as the norm and pure synthetic compounds should be used in place of raw materials that occur naturally which are used as precursors in manufacturing.

4. Having a tendency to exhibit the unique electrical property of superconductivity, mechanical properties like increased toughness and very high strength in temperature. These properties can be carefully processed and can undergo quality control precisely.

5. Having a design with micro structure and micro control in processing.

Hence technical or advanced ceramics are often treated as products with high added values.

Advanced or technical ceramics belong to one of several materials, such as glass, plastics and metals that can be used to protect the environment. These ceramics are also helpful in regenerating damaged ecosystems. The technology used to create these materials is known as environmental engineering [2].

6.2. CHARACTERISTICS OF ADVANCED CERAMICS

Aluminium Oxide (Al_2O_3), Silicon Carbide (SiC), Aluminium Nitride (AlN), Zirconia (ZrO_2), Silicon Nitride (Si_3N_4) and materials with titanium base are some advanced ceramics each having particular characteristics of their own. These materials exhibit high performance and act as an alternative in terms of economic parameter to regular materials like plastics, metal and glass. One of the important aspects of recent applications is to enhance low cost operation. In view of this adoption of new materials, the science and engineering meet the needs of unique and specific applications to gain significance. Ceramics can be joined to metals with special expertise. In this context it is required to remember worldwide company which is famous for metallisation and ceramic joining (Morgan advanced materials) that have worldwide customers. Morgan is expert in providing top most integrated solutions for components of any size, shape or specification. Any designer has to take into consideration the types of ceramic materials available. Many of the ceramic materials are highly favourable with excellent track record of electrical, chemical, mechanical and thermal properties. Consideration of physical parameters that include strength, hardness, wear resistance, thermal stability and corrosion resistance is very important while selecting a material. Optimization of above properties can be done based on the selected material. Examples include alumina, aluminium nitride, zirconia, silicon nitride *etc* [3 - 5].

6.3. TYPES OF CERAMICS

a. Alumina

One of the important materials with combination of good electrical and mechanical properties is alumina which is suitable for many applications that include X-ray and electron tubes, aerospace devices, laser devices, flow meters, applications related to high vacuum, pressure sensors and wear components *etc*. Alumina has high strength, resistance, stiffness and hardness. Its grade ranges from 60.0 to 99.90% along with additives designed to increase the dielectric strength. Formation of alumina is done with ceramic processing methods of different types. It is capable of processed into different shapes and sizes. Also, it is capable of getting joined to other metals or ceramics by using special techniques like brazing and metalizing [6].

b. Aluminum Nitride (AlN)

AlN exhibits good thermal conductivity, corrosion resistance and thermal shock resistance and Because of these properties AlN can be widely used in power and opto-electronics, aeronautical and railway systems, processing of semiconductors, defence and microwave applications. Specific applications include IC packages, heat sinks and heaters.

c. Zirconia (Zirconium Dioxide)

Zirconia (zirconium dioxide) is a ceramic which is a white powdered metal oxide. It is made from a metal zirconium having properties similar to titanium. Since it is chemically unreactive zirconium is an important choice for dental applications. The main advantage of zirconia is its capacity of exhibiting resistance at 2400°C

CHAPTER 7

Advanced Ceramics for Effective Electromagnetic Interference Shields

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Abstract: The electromagnetic (EM) interference is one of the major issues in EM wave applications. To prevent electronic devices from the EM wave interference, there is a need to find novel materials for shielding the EM wave interference. In this chapter, we discussed the EM wave interference and the effective EM interference parameters to find the strength of shielding. The chapter contains the mechanism and some derived materials reported by the various scientists. The materials are classified as ferrites, composites, and carbon-based materials. Herein, some other interesting materials like ferrites and conducting polymer composites were discussed to shield the EM interference.

Keywords: Dielectric loss, Electromagnetic Interference, Ferrites, Polymers, Shielding.

7.1. INTRODUCTION

Generally, the interference can be defined as the superposition of two or more waves thereby the modification of intensity. The modification contains minimum and maximum positions. If the waves are electromagnetic in nature, the applications of EM waves will be generally varied. The high-speed digital circuits and analog circuits of electronic systems are accounted for as major problems of electromagnetic interference (EMI). In recent years, the large-scale usage of elect-

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ronic systems in different fields, electromagnetic microwave interference is emerging as a new class of environmental pollution. It is creating significant damage to electronic devices and biological things like the human body and all the environmental species. In order to reduce the electromagnetic wave interference, to keep the human body and clean environment away from EMI radiation, considerable research has been focused on the improvement of composites such as ferrites, polymers and inorganic materials which are capable to absorb the microwave radiation thereby electromagnetic shielding capacity [1]. In last decade, a number of ideas were developed to reduce this type of EM pollution. These ideas include shielding, arranging the components of electronics as keeping away from radiation. The usage of embedded capacitance and components drop more data throughout the system. Among these methods, the preparation of shielding materials is the most useful method [2]. The consumption of the materials in regular life and industrial purposes depends on the constant supply of those materials.

Day by day, the consumption rate is growing exponentially owing to increase of population. Hence, for the sustainable future, it is important to find new ways to use those materials effectively. At present, the global attention is to overcome the challenges for sustainable advancement in materials. For this purpose, the industries forced to conduct self-assessment to identify the strategies and opportunities to achieve this goal. In addition, the strategy for the environmental sustainability is a long-term view *i.e.*, adjustment of the life style which meets the present requirements deprived of compromising the requirements of future generations. Due to continuous increasing demands for the ecofriendly products, particularly on dealing with products end of life phase, product designers and manufacturers are essential to consider the future disposal of their products. Further, well functioned recycling techniques were existed for the traditional materials like aluminium and steel. But these are not suitable for more extensively used structures of composites [3]. This is attributed to a fact that the composite material consists of several types of materials as a mixture on macro level. They may not be considered as homogeneous as the steel materials. These situations obscure the opportunities to form an efficient approach for waste management. Even though, several methods are existed, they are not commercially available. Landfill and incineration are the present disposal techniques of composite materials. Besides, many investigations are pointed out recycling of composite materials as the best alternative considering environmental effects. Exclusively, recycling of polymer composites is significant method to obtain complete information about the elements of these materials.

As discussed above electromagnetic microwave interference is being emerging as a new class of environmental pollution creating a significant damage to electronic applications and the biological things like human body and all of environmental species [4]. In order to target the electromagnetic interference, to keep safe from damages of equipment, keep the human body and clean environment far away from EMI radiation, a considerable research is being focused on the improvement of composites and materials. They are ferrites, polymers and inorganic materials which have capable to the microwave absorption and electromagnetic shielding capacity. Apart from these electromagnetic parameters, the high abundance of physical and morphological parameters such as low density, porous structure and multiple polarization centers can enhance the microwave absorption property. The high magnitude of the above said parameters can give rise to the multiple reflection and scattering of microwaves thereby matching the impedance [1, 3]. From the vast literature survey, it was evidenced that the ceramic materials belonging to the spinel ferrites, magnetic spinels, hexaferrites, magnetic perovskites, ceramic composites and ceramic polymer composites showed the high microwave absorption efficiency [2]. In view of this, the nickel zinc ferrites, nickel zinc cobalt ferrites, nickel cobalt zinc lanthanum ferrites, nickel zinc lanthanum ferrites, manganese zinc ferrites, barium zinc cobalt U-hexaferrites, barium hexaferrites, aluminium titanate and lanthanum iron oxide offered considerable microwave absorption behavior at giga hertz frequency range [2]. Once the microwave absorber materials are exposed to the EM radiation, EM radiation enters the interior of material. Later on, the electromagnetic radiation will be absorbed and transformed into dissipated energy. Therefore, the electronic object will be prevented from EMI. A photograph of microwave absorber is provided in (Fig. **7.1**) [5].

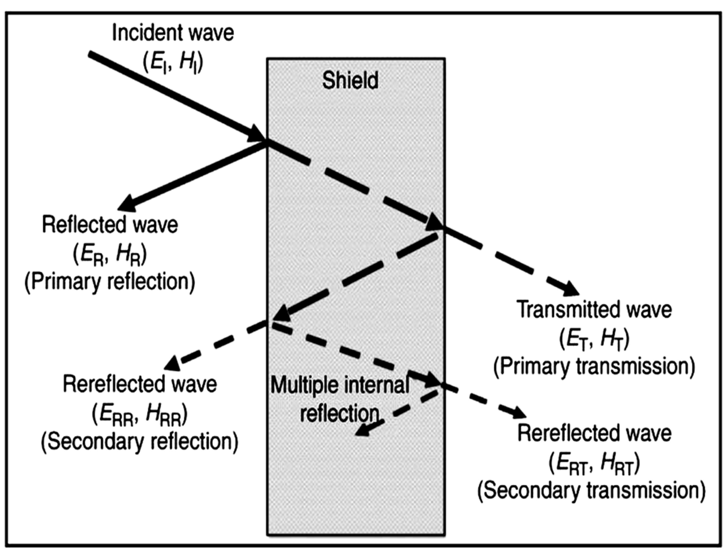

Fig. (7.1). Shielding mechanism of electromagnetic waves at the boundary.

CHAPTER 8

Advanced Ceramics for Ferroelectric Devices

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Abstract: The presence of intrinsic polarizations into the ferroelectric materials helps them to get polarized easily on the application of the electric field. The presence of the retentivity and the coercivity formed a hysteresis loop pattern when the field is applied to the materials. But some artifacts make the nature of such a hysteresis loop distorted for the ferroelectric materials. In general, the non-centrosymmetric nature of the crystal structure responsible for the ferroelectric nature of the materials. That is why the presence of the intrinsic polarization in the electrets does not make it a ferroelectric class of materials. Actually, the ferroelectrics come under the dielectric class of materials. The present-day application of the ferroelectric materials ranges from the ferroelectric memory devices, electro caloric devices, magneto electric devices, DRAM capacitors, *etc*. The flexible properties along with the high writing speed and cyclability make $Bi_{3.25}La_{0.75}Ti_3O_{12}$ as one of the most promising materials for FERAM applications. The large ECE values of the Barium hafnium titanate makes it very useful for the electro caloric cooling of the microelectronics devices. The presence of both spin glass state as well as the ferroelectricity make advanced ceramics like $La_3Ni_2NbO_9$ couple both magnetic and electric field within the same material for the fabrication of the magneto-electric devices. The presence of a morphotropic phase boundary in the advanced ceramics of hafnium oxide and zirconium oxide can result in a high dielectric constant for the DRAM applications.

Keywords: Ceramics, DRAM, Ferroelectric Materials, Magneto-Electric Devices, Magnetic loss.

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8.1. INTRODUCTION

Ferroelectrics are the class of material with intrinsic polarization and this polarization can be tuned in accordance with the applied electric field [1 - 4]. When the external field is applied the polarization keeps on increasing due to the alignment of the electric dipoles along the direction of the applied fields [5]. When all the dipole alignment completes the polarization get saturated although the increase of the applied fields. But on the field reversal the material does not follow the same path and trace a loop known as the hysteresis loop [6 - 10]. But due to different artifacts the hysteresis loop can be different from their magnetic counterparts. For example, electrets normally build with melting the plastic or glass and thereafter polarized with applied external electric fields can also show a hysteresis loop but they can never be treated as ferroelectrics [11 - 13]. It is commonly known facts that although all the ferroelectrics dielectrics are insulators but we can treat all the insulators as dielectrics.

Actually, the dielectrics can be classified in different types for example ferroelectrics, pyroelectrics, piezoelectrics *etc*. Here the ferroelectrics are the core part of the all dielectrics. For instance, zinc oxide is a well-known pyroelectric material but it is not a ferroelectric material [14 - 16]. But on the other hand, barium titanate is a very popular ferroelectric materials hence by default it is also pyroelectric and piezoelectric in nature [17 - 20]. Hence, we cannot claim that there exists a center of symmetry for the ferroelectric material nor they are just simple glass material. Due to these features the ferroelectric hysteresis loop always comes with distorted shapes due to the losses along the artifacts.

In the earlier days soon after the discovery of ferroelectric materials in 1920 by Valasek people start believing that the hydrogen bond is the responsible factor. The reason for that was the water-soluble nature of the earlier days of ferroelectrics. But with the discovery of barium titanate in 1943 the real physics of non-centrosymmetric design of the ferroelectric start coming into the picture. Gradual shift of research towards ferroelectric thin film and there after successful integration to silicon chips a wide new area called ferroelectric memory devices comes into light in the year 2000 onwards. Not only ferroelectric memory devices [21, 22] we can see advanced ceramics applications in electro caloric devices [23, 24], magneto electric devices [25, 26], DRAM capacitors [27, 28], magnetic field sensors [29, 30], electron emitters [31, 32] and spatial light modulators [33, 34] *etc*. So, in this book chapter we will focus to understand the role of different ferroelectric ceramics for the device applications.

8.2. FERROELECTRIC MEMORY DEVICES

The uses of PZT and SBT are well known in the fabrication of nonvolatile ferroelectric random memory devices. But we will discuss here some advanced ferroelectric materials like $Bi_{3.25}La_{0.75}Ti_3O_{12}$ for such applications.

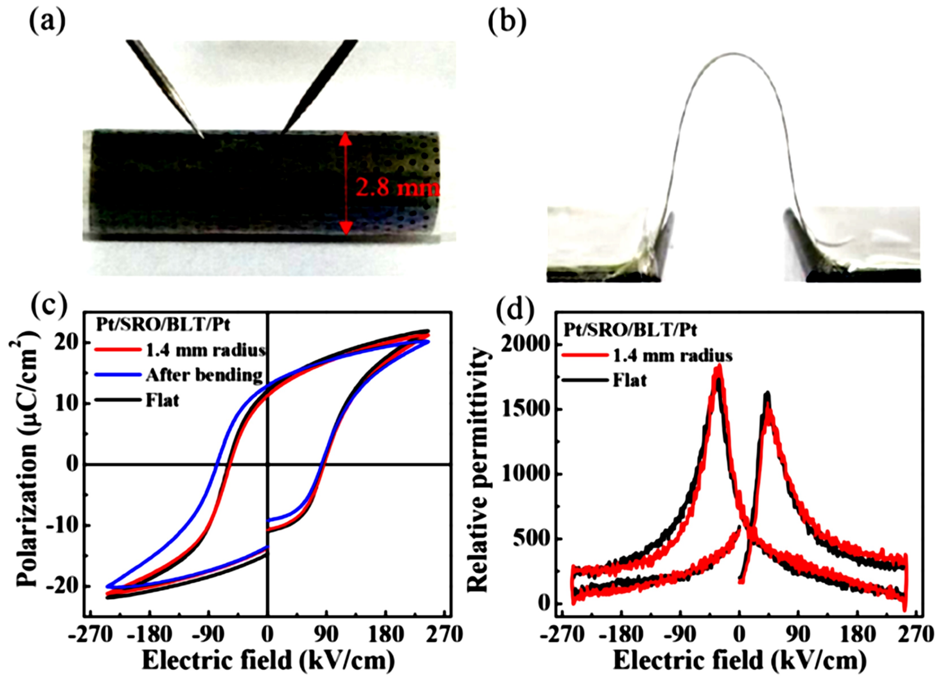

Fig. (8.1). (a & b) Sketches **(c)** P-E loops **(d)** ε_r-E curves of mica/Pt/SRO/BLT/Pt memories. Reprint with the permission from Ref [35]. Copyright 2018, ACS Publishing.

8.2.1. $Bi_{3.25}La_{0.75}Ti_3O_{12}$

Although, PZT films are very popular but they are, in general, fabricated in a silicon substrate that makes the films nonflexible. Hence for advanced flexible ferroelectric memory devices applications the used of PZT films are in general unsuitable. Hence the use of new advanced materials like MoS_2 is gradually coming into action. But there are certain drawbacks in these materials such as slow writing speed as well as lower cycles of use. Hence, very recently a new advanced ceramic material of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ reported for flexible FERAM application purpose shown in Fig. (**8.1**) [35]. Here the mica has been used as substrate and Pt/$SrRuO_3$ used as electrodes. The thickness of the substrate can be reduced as thin as ten micron which enhanced the capabilities of the FERAM devices. Hence the fabricated device can withstand higher strain as well as the

CHAPTER 9

Transport Properties of Semiconducting Glasses: A Review

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Abstract: Research related to amorphous semiconductors in thin films has gained tremendous significance due to their applications in potential areas. Lead vanadate that belongs to the category of semiconducting oxide glasses has been studied to the extent of consideration. Apart from their application point of view, it is necessary to understand the physical properties of these materials. Taking into consideration wide variation in material composition, it is evident that large scope prevails in terms of research. Many laboratories were carrying extensive research on binary, tertiary mixed metal oxide glasses along with their derivatives/substitution of other metal oxides or transition of rare earth metal oxides was identified to suit for glass system showing considerable variation in physical properties if substituted for different applications. A review on these glass systems has been reported in this paper in particular transport properties of semiconducting glasses.

Keywords: Ceramics, Metal Oxides, Semiconducting Glasses, Transition, Transportation.

9.1. INTRODUCTION

The study of amorphous materials is very interesting because of their peculiar character in contrast to the crystalline materials. In recent times more emphasis on the scientific study of these materials increased because of their technological importance or promise. Though a large number of investigations have been made on these non-crystalline materials, a large part of the physical properties is still to be understood. The wave-like nature of the electron in a periodic potential of a crystalline lattice was invoked to develop the band theory for better awareness related to their physical properties.

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But the absence of the long-range periodicity in amorphous materials makes this task rather complicated. In amorphous materials, atomic arrangement do not have periodicity (long range order) found in the crystalline materials. However short range order exists. These materials possess randomness which can exist in different forms like spin, topological, vibrational or substitutional disorder. (Fig. **9.1**) [1] shows the topological disorder. Amorphous materials that exhibit the phenomenon of glass transition are referred to as glasses. A material formed by cooling from molten state and exhibiting zero discontinuous changes in first order thermodynamic parameters is known as glass.

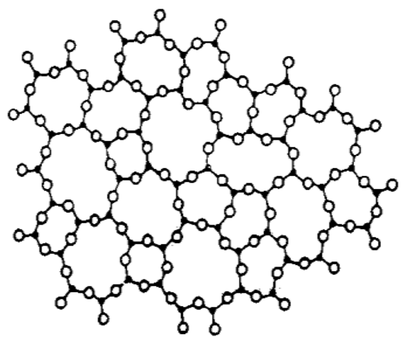

Fig. (9.1). Two dimensional continuous random networks as proposed by Zachariasen (taken from S.R. Elliot) [1].

9.2. GLASS TRANSITION

The transition from a liquid to glassy state is denoted by glass transition. In the liquid state a substance flows under any shear stress and its structure a change with changing temperature. In the glassy state, the substance, a glass, is solid. It does not flow irreversibly, and the structure is frozen. A glass has a molecular structure with order in a short range (a few molecular dimensions), but no long-range order at many molecular distances. (Fig. **9.2**) [2] shows schematically the change in volume V, enthalpy H, or entropy S of a liquid during cooling. For substances which can exist in both glassy and crystalline states, there are two possible paths below the melting temperature T_m. One of these paths is the usual one for crystalline solids below T_m and the other is a super-cooled liquid below $T_{m.}$

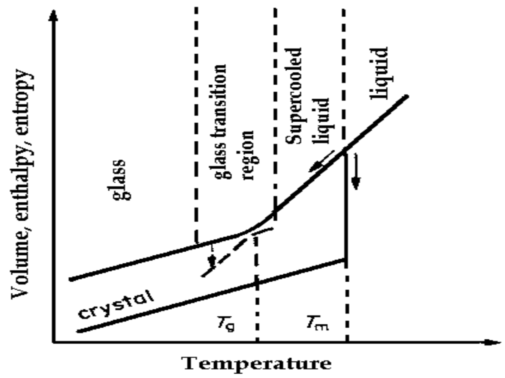

Fig. (9.2). Temperature dependence of properties of liquid, glass and crystal.

$$\partial G / \partial T = -S \qquad \textbf{(9.1)}$$

where G is the Gibbs free energy.

It follows from (Fig. **9.3**) [3] that to form a glass, the liquid must make a thermodynamically un-favorable choice and follow the path with higher free energy, for kinetic reasons. At the temperature T_m, crystallization is impeded by a finite viscosity of the liquid. By rapid cooling, crystallization is kinetically arrested. Inorganic glass forming melts have a high viscosity at T_m and can be cooled slowly. In contrast, molten metals require cooling rates of the order of 10^5 K s^{-1} to form glass. An expression relating T_g and cooling rate derived from free-volume theory is given by:

$$q = q_o \ \exp\left[-1/C\left(1/T_g - 1/T_m\right)\right] \qquad \textbf{(9.2)}$$

CHAPTER 10

Advanced Ceramics for 3D Printing Applications

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Abstract: Additive method is employed for 3D printing ceramic materials over a subtractive conventional method with the help of computer-aided design [CAD]. The different feedstocks are used to print ceramic materials such as slurry, powder and bulk solid. Alumina powder is the most common material and excellent oxide used as a catalyst, adsorbent, aerospace material and microelectronics material. With the help of stereolithography technique, glass ceramics and active glass can be printed.

Keywords: Active Glass, Alumina Powder, CAD, Glass Ceramics, Stereolithography.

10.1. INTRODUCTION

Ceramics in a broader concept includes all silicates. The word is derived from the Greek word keramos meaning burnt stuff. Ceramics refer to clay products such as porcelain wares, potteries, refractories, building bricks, insulating materials, *etc*. ceramics is also referred to as inorganic nonmetallic materials processed at high temperatures. The basic raw materials required for the manufacture of ceramics are clay, feldspar, sand or quartz. Ceramic is strong, durability and fire-resistant. The history of ceramics in India dates back to Hindus valley civilization and ceramic materials or articles were prepared by their own traditional methods, during that period, people used the pots for the preparation of food, preservation of grains, *etc*. so, from this, we can say that ceramics or pottery are very ancient

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and tool for effective civilization of society. Still in India the pot making is very good cottage industry in Indian village setup. Now a good transition took place in the ceramics, called 3D printing technology, in this technology ideas or dreams become materials with the help of CAD (computer aided designing) *i.e.*, geometrical figures can be processed into desired materials. Compare to traditional method, 3D printing has a high potential to ensure rapid preparation of materials. This technology Prints more complex materials or structures than conventional or traditional materials. This 3D printing is also called as rapid proto typing or additive manufacturing, in this technique the materials are formed by number of layers. In 1980's the first material was prepared at Nagoya municipal industrial research institute. Now varieties of 3D printing materials are printing such as nanomaterials, bio materials, smart materials and membranes and even extended the applications of 3D printing materials in the constructions, heart pumps, aerospace, biomedical, food industry and *etc* [1].

Most commonly used material is alumina powder is excellent ceramic oxide form which is used in catalysts, adsorbents, microelectronics, chemicals and aerospace industry. Stereolithographic machine is used to process glass ceramics and bio active glass and it improves bending strength of the materials [2]. Technology that is preprocessed feedstock before printing generally classified into slurry based, powdered based, and bulk solid based methods that is given in the below Table **10.1**. The viscosity range in slurry-based technology in ceramics/polymer mixtures from low-viscosity (~m Pa· s) inks with a low ceramic loading (up to 30 vol %) to high-viscosity (~Pa· s) pastes with a much greater ceramic loading (up to 60 vol %) [3].

Table 10.1. Technology behind various feedstock forms.

Feed Stock Form	**Ceramic 3D Printing Technology Type**
Slurry based	Stereolithography [SL] Digital light processing [DLP] Two-photon polymerization [TPP] Inkjet printing [IJP] Direct ink writing [DIW]
Powder based	3-dimensional printing [3DP] Selective LASER sintering [SLS] Selective LASER melting [SLM]
Bulk solid based	Laminated object manufacturing [LOM] Fused deposition modeling [FDM]

The direct ink writing possesses a great application in 3D printing, in the preparations of sensors, electrodes, energy storage, tissue engineering scaffold, and shape morphing system. In this process the most critical one is maintaining the appropriate viscosity and elastic porosity of ink [4]. The digital light processing is also playing an important role in the preparation of meshes for 3D printing materials, that meshes or whiskers are used in the separation of water or oil [with the help of honey comb mesh] and also used to purify oil. This technique is based on the light-curing of light sensitive reaction to produce layer by layer printing and accomplish. From this DLP approach (Table **10.1**), ceramic phosphors also can be prepared for high flux LASER light that is used to fabricate LASER diode which possess high power density due to thermal endurance and thermal stability of luminescence, the material used for this laser is an Al_2O_3/YAG: Ce^{3+} [5, 10, 11]. The working diagram of DLP is as shown in Fig. (**10.1**) [5]. More ecofriendly and naturally occurring polymers are used in the preparation of ceramics one of them is methyl cellulose [MC] which possess low concentration. This methyl cellulose with magnesium aluminate [$MgAl_2O_4$] spinel is used to prepare transparent materials which are generally used in transparent windows and domes, and this spinal is very good refractory. This spinal possesses many bio medical applications such as artificial bones, teeth, hemispherical hip and *etc* [6].

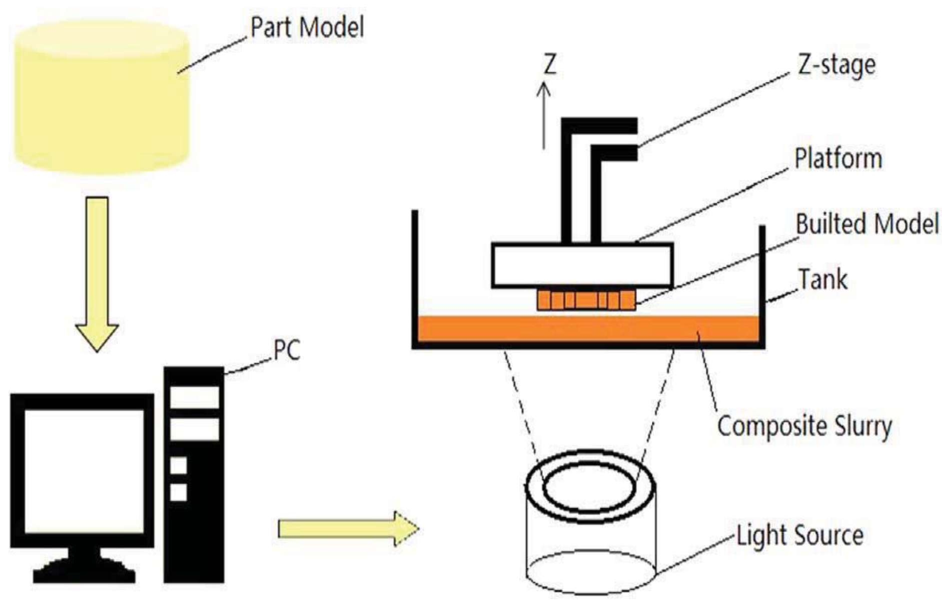

Fig. (10.1). Working diagram of DLP.

In bone making this 3D printing is used (Fig. **10.2**) [7], the materials which are used in bone making are calcium phosphate materials which are similar to our

CHAPTER 11

Advanced Ceramics for Biomedical Applications

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Abstract: Bio ceramics are being prepared by advanced 3D printing technology which is a very good economical technique. Different inorganic materials can be used to print bio ceramics for different applications such as alumina, zirconia, Leucite, lithium disilicate and mica-based ceramics. The main implications of bio ceramics are in dentistry and orthopedics.

Keywords: Alumina, Bio Ceramics, Dentistry, 3D printing, Orthopedics, Zirconia.

11.1. INTRODUCTION

Ceramics played a pivotal role in the civilization of man since time immemorial. Before ceramics invention, man was nomadic for his food because of storage specialties were not in existence. In later period, these ceramics were used as a storage appliance to store their food materials, so ceramic appliances stop nomadic life of man and settlement took place in his desired places. Now ceramic applications pervaded into all spheres of human life from pottery to medicine domain. As a result of scientific research in the field of ceramics from the last five decades, bio ceramics came into medical field. The ceramics intending to contact with living tissue is called bio ceramics which are used to replace damaged part in a human body, generally in orthopedic and dentistry. These ceramics generally composed of inorganic compounds with ionic and covalent bond. Their mechan-

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ical properties are good in agreement with natural things, such as great compression strength, very low tensile strength, very stiff, brittle and high young's modulus. The surface properties of bio ceramics have more advantages of high wetting properties and high surface tension which helps to accumulation of proteins, cells and other biological moieties. Alumina, zirconia, calcium phosphate and glasses and glass ceramics are the good examples of bio ceramics. Now research is going on to develop organic-inorganic composition bio-ceramics called hybrid ceramics. The bio-ceramics are relatively strength, low conductivity of heat and electricity and high melting point, the carbon element is treated as ceramic as it possesses many ceramic properties [1].

The manufacturing of bio ceramics is by the method of 3D-printing or additive manufacturing [AM], in this manufacturing no wastage of ceramic material takes place, but in traditional method called subtractive manufacturing [SM] the wastage of materials happens and also time consuming with more manufacturing cost [2]. Bio ceramics are widely used in dentistry and the most of the properties of these materials similar to natural dental material. Bio-ceramics are broadly classified into four categories such as follows:

Glass based systems mainly comprising silica;

Glass based systems mainly comprising silica with fillers, generally crystalline based;

Crystalline based systems with glass fillers;

Poly crystalline solids.

The glass-based systems contain mainly silicon dioxide with different amounts of alumina, feldspars comprise of aluminosilicates occur in nature with different proportion of potassium and sodium. Glass based systems with fillers consists of large range of glass crystalline ratios and crystal type. Crystalline based systems with glass fillers contains glass infiltrated and partially sintered alumina, first introduced in 1988. Polycrystalline solids prepared by sintering crystals form a dense, air free, glass free poly crystalline structure.

The following materials are commonly used, in order to prepare bio-ceramics such as

Zirconium based ceramics (ZrO_2);

Alumina based ceramics (Al_2O_3);

Leucite based ceramics ($K[AlSi_2O_6]$);

Lithium di silicate glass ceramics ($Li_2Si_2O_5$);

Mica based ceramics.

11.2. ZIRCONIUM BASED CERAMICS

These engineering materials are very much popular because of their mechanical properties: fracture toughness, elastic modulus and wear resistance. Yttrium stabilized zirconia (YSZ) possess good implications by superior combination of mechanical properties YSZ will be used as an implant in human body.

11.3. ALUMINA BASED CERAMICS

Alumina based ceramics shows good strength and hardness with excellent wears resistance properties but low fracture toughness. The strength and toughness of the material can be improved by adding tetragonal Zirconia particles.

11.4. LEUCITE BASED CERAMICS

It is potassium alumina silicate-based material with tetragonal structure at room temperature. At higher temperature about 625ºC transition takes place from tetragonal to cubic structure. Leucite is implicated in dentistry.

11.5. LITHIUM DISILICATE BASED CERAMICS

This material also shows a good strength, hardness and excellent wear and tear resistance properties. By virtue of mechanical strength and optical properties they are used in single and multiunit dental restoration such as dental crowns, bridges and veneers.

11.6. MICA BASED CERAMICS

Mica minerals are group of silicate minerals that may be in the layered form. The mechanical properties are depending on specific crystal structure formed by cleavage of planes which are located along the planes [2, 3]. The bio ceramics can be used in tissue engineering and biomedical science and bio active glass are third generation bio material and excellent bio compatibility, degradability and bio activity. The bio active glass can form the bone bond through apatite on the surface layer and induce angiogenesis. And the size of the particle of bio glass are very small and high surface area which gives rise high surface to volume ratio leads to good cell attachment used in drug delivery and also used in soft and hard tissue generation. In order to improve mechanical strength of the bio active glass, other elements can be injected such as graphene and graphene oxide nano particles due to their optical, electrical and mechanical properties [4]. In bio

CHAPTER 12

Advanced Ceramics for Antimicrobial Applications

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Abstract: In this chapter, we specified the origin of ceramics, historical background along with advantagesof the ceramic materials. Meanwhile, the classification of ceramics was also mentioned in a detailed manner. With special interest, we focussed on the antimicrobial applications of advanced ceramics followed by detailed and tabulated data.

Keywords: Antimicrobial Applications, Cell Membrane, Ceramics, Microorganism, Oxidative Stress.

12.1. INTRODUCTION

Generally, the ceramic word came from the Greek language as keramos, and its meaning was “pottery”, which was expressed as “to burn” in an ancient language of Sanskrit. Although, the Greeks used the ceramic word to “burnt stuff or “burned earth”. This was associated with the function of fire over earthly things. In order to prepare the inorganic and nonmetallic substances, the solid articles were considered based on the art and science of making and usage of the ceramics. According to this, not only the materials like structural clay products, pottery, refractories, porcelain, porcelain enamels, abrasives, cements, and glass, but also nonmetallic magnetic materials, ferroelectrics, and a variety of other products like oxides, carbides and nitrides *etc*., can be used. United States acquired about ten billion dollars per annum by the ceramic industry. The ceramic industry played a pivotal role in development of many other fields. For instance, refractories are a primary component of the metallurgical industry. Abrasives are crucial to the machine tool and automobile fields. Further, the products of glass ceramics were stipulated to the automobile industry along with electronic and ele-

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ctrical industries. Cements are needed to the building and architectural industry. Numerous electrical and magnetic ceramics are important to the advancement of computers and electronic control devices. In view of every industrial production and everyday applications of human beings, ceramic materials play significant role. The recently fabricated devices are excluded with ceramic materials owing to their suitable structural, mechanical, electrical, thermal and chemical properties. Finally, the complexity and utility of the materials may exhibit better improvement of their properties in a magnified and tremendous way. In addition to this, many other applications are noticed due to their bigger and greater quality of functioning of the entire system. For better understanding of the ceramics properties the intensive research has been the best path way.

12.2. HISTORICAL PERSPECTIVE

Ceramics were investigated by several archaeologists at the time of 24,000 B.C. Czechoslovakia was first person to find the materials in the form of human and animal figurines, slabs, and balls. The ceramics are made up of the animal fat and one bone combined with other bone ash and the fine clay-like materials. Whenever the ceramics were heated between the range of 500-800^{o}C in domed and horseshoe shaped kilns of partially dug into the ground with walls. During the time of 9,000 B.C, the functional pottery vessels were used in the first time. These were used to store and preserve other food products. Meanwhile, the manufacturing of glass also developed in Upper Egypt at the time of 8,000 B.C. Basically, the pottery holds the calcium oxide (CaO). But during the process of overheating of pottery kiln can be taken in a colored glaze on the ceramic pot. It is known that the ceramic glass preparation was not done comfortably until 1,500 BC. That is, latter, the glass was developed independently using ceramics and fashioned into different items. On the basis of clay-water system, many other traditional ceramics were developed although it was the only first broadly analyzing colloidal system with respect to many advertised ceramic texts. To enable and engineered the ceramic suspensions, the joining of organic processing additives *via* polymer and plasticizers with distinct clay-based system. Moreover, these are the reasons for taking part of the modifications in the rheological behavior and impart handling force to as-formed ceramic texts.

12.3. CLASSIFICATION OF CERAMIC MATERIALS

The Ceramic substances can be classified as follows:

Crystalline ceramics: Which includes silicates, oxides, nonoxides compounds.

Glasses: These are non-crystalline solids which may be silicates or nonsilicates.

Glass-Ceramics: These are primarilymolded as glasses followed by crystallization through controlled heat treatment.

Carbon materials: These include graphite, diamond, fullerenes and nanotubes.

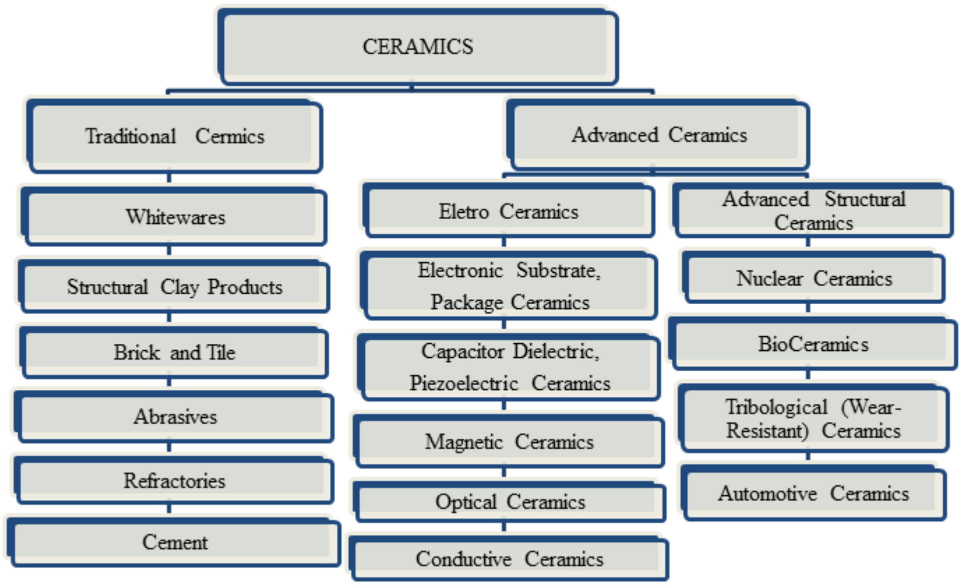

Fig. (12.1). Classification of ceramic materials.

Although Ceramics can also be divided into two parts: (i) Traditional ceramics and (ii) Advanced ceramics, the following (Fig. **12.1**) represents the classification of ceramic materials. The word 'advanced' can be treated as 'technical', 'special', 'fine' or 'engineering'. The traditional ceramics hold a closer association with the previous materials, whereas the first civilization society such as pottery, structural clay products, and clay-based refractories, used the items consisting of cement, concretes and glasses. Eventually, the traditional ceramics played a crucial role in ceramic industry for last few decades and later on, these were concentrated towards the advanced ceramics. The advanced ceramics were developed since last 5 decades. Advanced ceramics consist of ceramics exhibiting the significant electrical, magnetic, electronic, and optical applications. Although traditional ceramics are responsible for the bulk materials, both in tonnage and in dollar volume, a variety of new ceramics have been developed in the last 50 years. These peculiar properties are depending on their special interest with reference to specific requirement in better temperature resistance, greater mechanical

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