

**MECHANICAL PROPERTIES AND
CYTOTOXICITY STUDIES OF CALCIA
STABILIZED ZIRCONIA (Ca-SZ) FOR DENTAL
APPLICATION**

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**MECHANICAL PROPERTIES AND CYTOTOXICITY
STUDIES OF CALCIA STABILIZED ZIRCONIA (Ca-SZ)
FOR DENTAL APPLICATION**

by

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LIST OF SYMBOLS

°	Degree
°C	Degree Celsius
θ	Theta
%	Percentage
σ	Sigma
λ	Wavelength
π	Pi
™	Trademark
±	Plus Minus
μ	Micro

LIST OF ABBREVIATIONS

SEM	Scanning Electron Microscope
EDX	Electron Dispersive X-ray
g	Gram
ISO	International Organization for Standardization
M	Molar
ml	Millilitre
mm	Millimetre
MPa	Mega Pascal
nm	Nanometer
rpm	Rotation per minute
s	Seconds
SD	Standard Deviation
ASTM	American Society for Testing and Materials
cm	Centimetre
CAD/CAM	Computer Aided Design/ Computer Aided Manufacturing
FDPs	Fixed Dental Prostheses
CaO	Calcium Oxide
ZrO ₂	Zirconium Oxide
HGF	Human Gingival Fibroblast
Ca-SZ	Calcia-Stabilized Zirconia
Y-TZP	Yttria-stabilized Tetragonal Zirconia Polycrystal
MgO	Magnesium Oxide
ICDS	Inorganic Crystal Structure Database
XRD	X-Ray Diffraction

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- Appendix A Manual Instruction of CEREC Sirona, The Dental Company
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**CIRI MEKANIKAL DAN KAJIAN SITOTOKSITI ZIRKONIA
DISTABILKAN CALCIA (Ca-SZ) UNTUK APLIKASI PERGIGIAN
ABSTRAK**

Terdapat beberapa kajian mengenai penggunaan zirkonia dalam aplikasi pergigian, tetapi hanya sedikit yang menggunakan kalsium oksida (CaO) sebagai penstabil. Aspek mekanikal dan kajian sel tidak mencukupi, meninggalkan kesan dalam bukti mengenai sifat mekanikal dan biokompatibiliti Ca-SZ sebagai bahan pergigian. Sintesis CaO daripada nitrat kalsium tetrahidrat digunakan sebagai pendahulu logam untuk menghasilkan Ca-SZ. Bioseramik Ca-SZ disinter pada tiga suhu yang berbeza iaitu 1200°, 1300° dan 1400°C. Ca-SZ dikaji menggunakan Mikroskopi Elektron Imbasan (SEM), Analisis Spektroskopi X-ray Dispersi Tenaga (EDX) untuk analisis unsur, dan X-ray Difraksi (XRD) untuk kajian komposisi. Sampel Ca-SZ menunjukkan morfologi yang baik di bawah pengamatan SEM. Peningkatan suhu pembakaran meningkatkan morfologi permukaan, fasa Ca-SZ menjadi lebih intensif dan berubah dari zirkonia monoklinik kepada zirkonia tetragonal, dan kekuatan lentur meningkat. Sifat mekanikal untuk Ca-SZ pada suhu 1400°C menunjukkan keputusan yang baik dibandingkan dengan CEREC Zirconia komersial. Biokeramik Ca-SZ yang disinter pada 1400°C mempunyai kekuatan mekanikal yang sebanding terutamanya berkaitan dengan fleksural yang mencapai 535.3 MPa manakala CEREC Zirconia mencapai 683.18 MPa dan kekuatan retak 4.73 MPa m^{1/2} berbanding dengan CEREC Zirconia 4.91 MPa m^{1/2}. Kesan viabiliti tertinggi Ca-SZ adalah pada inkubasi 24 jam yang mencapai 95% sebanding dengan CEREC Zirconia pada 97%. LogIC50 Ca-SZ pada inkubasi 24 jam adalah 0.20417 mg/ml dan sebanding dengan CEREC Zirconia pada 0.1995 mg/ml. Pembangunan Ca-SZ boleh bertindak sebagai bahan alternatif untuk aplikasi pergigian.

MECHANICAL PROPERTIES AND CYTOTOXICITY STUDIES OF CALCIA STABILIZED ZIRCONIA (Ca-SZ) FOR DENTAL APPLICATION

ABSTRACT

Several studies can be found on zirconia as dental application but only few of them use calcium oxide (CaO) as its stabilizer. Mechanical aspects and cell studies were not covered, leaving a gap in the evidence regarding the mechanical properties and biocompatibility of Ca-SZ as dental materials. CaO synthesis from calcium nitrate tetrahydrate was used as metal precursor to produce Ca-SZ. Bioceramic Ca-SZ was sintered at three different sintering temperatures 1200°, 1300° and 1400°C. Ca-SZ was characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX) element analysis, X-ray Diffraction (XRD) for composition studies. Ca-SZ sample shows a good morphology under SEM observation. Increment of sintering temperature enhance the surface morphologies, the phase of Ca-SZ become intensified and transformed from monoclinic to tetragonal ZrO₂ and the flexural strength increases. The mechanical properties for Ca-SZ at temperature 1400°C displayed a good result that was comparable with commercial CEREC Zirconia. Ca-SZ bioceramic sintered at 1400°C had comparable mechanical strength especially with regard to flexural that reach up to 535.3 MPa while CEREC Zirconia goes up to 683.18 MPa and fracture toughness 4.73 MPa m^{1/2} as that of CEREC Zirconia 4.91 MPa m^{1/2}. The highest viability of Ca-SZ was at 24 hours incubation that reached 95% comparable with CEREC Zirconia at 97%. The LogIC₅₀ of Ca-SZ at 24 hours incubation was 0.20417 mg/ml and comparable with CEREC Zirconia at 0.1995 mg/ml. The development of Ca-SZ can act as an alternative material for dental applications.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Biomaterial products from various background have been used widely to imitate the original feature like bone and tissue structure in human body. Biomaterials like natural or synthetic polymers, metals, composites, bioactive glasses and ceramic have been developed as dental application (Khalid *et al.*, 2017). The usage of ceramics like zirconia have been studied deeply to develop better crown and bridge formation in dental application. The utilization of zirconia for dental restoration applications is thought to have been in implementation since 1998.

Besides, the study of zirconia as dental restoration application has been explored widely because of impressive mechanical properties of zirconia such as good wear ability and friction as well as high mechanical strength (Chevalier, 2006; Denry & Kelly, 2008). In addition, zirconia consist high strength promoted the usage as load supporting application for dental applications for example dental crowns, fixed partial dentures (FPD) and dental implant. The fabrication of dental ceramics for dental restorative purposes required few technologies also techniques like injection moulding, slip casting, ceramming, thermal pressing and machining using technology that involves Computer Aided Design and Computer Aided Manufacturing (CAD/CAM).

Pure zirconia exhibits polymorphism material that consists of three different crystallographic structures based on the temperature of the material. It also called as allotropy phenomena due to the same chemical composition have different atomic arrangement and structure (Bajraktarova-Valjakova *et al.*, 2018). The three crystallographic phase structures of zirconia are known as structure monoclinic (M) at room temperature, shifting to tetragonal (T) at 1170°C and further transitioning to cubic (C) once reach 2370°C. However, crack propagation is easily induced during phase transformation. Therefore, addition of metal oxide (MgO_2 , CaO_2 , CeO_2 , Y_2O_3) to zirconia as stabilizer is essential to produce good molecular stability product (Mughtar *et al.*, 2012). It also creates multiphase material known as Partially Stabilized Zirconia (PSZ).

There are three categories of zirconia that are usually used in dental restoration application specifically, zirconia-toughened alumina (ZTA), magnesium partially stabilized zirconia (Mg-PSZ) and 3Y-TZP. The usage of Mg-PSZ, ZTA and 3Y-TZP have been used widely in production of crown and bridge for dental restoration applications supported by various clinical tests. However, currently there is only usage of 3Y-TZP that was remarkable compared to other doped zirconia.

The usage of other metal oxides like CaO can be developed as newly stabilized zirconia for dental application. Therefore, the production of calcia stabilized zirconia (Ca-SZ) by using in-house production was used in this study to produce the stabilized zirconia with CaO. The compatibility of Ca-SZ was analysed by material characterization and mechanical test that compared with commercial 3Y-TZP.

1.2 Problem Statement

The characteristics of Calcia Stabilized Zirconia (Ca-SZ) in terms of mechanical and the material characterisation were compared with current zirconia stabilizer like 3Y-TZP. The usage of 3Y-TZP as crown and bridge material may give problem during milling during repair and their removal due to high mechanical strength as its flexural strength reaches 900-1200 MPa (Alfawaz, 2016). The high mechanical strength of 3Y-TZP may make them hard to mill for its production, and also make it difficult to cut during repair. Besides that, the sintering temperature and period play crucial role to determine the grain sizes which influenced the mechanical strength. Incorporating CaO as a stabilizing agent has the potential to enhance the mechanical characteristics of zirconia, rendering them more compatible with dental applications.

Hussein *et al.* (2020) successfully fabricated and characterized zirconia doped with calcium oxide (CaO). The synthesized CaO derived from cockle shells, enhancing the biocompatibility of the materials by utilizing a natural waste resource. Cockle shell-based Ca-SZ was compared with commercially available Ca-SZ. The density measurements revealed that the Ca-SZ samples became more compact as the sintering temperature increased. The denser and more compact materials exhibited lower porosity, indicating good mechanical properties (Hussein *et al.*, 2020). Both categories of Ca-SZ samples demonstrated favourable mechanical properties, suggesting their potential to closely match Y-TZP.

In a previous study by Nur *et al.* (2020), the synthesis of Ca-SZ using the sol-gel method was successful. The samples underwent characterization, including physical tests such as density measurement, transmission electron microscopy (TEM),

scanning electron microscopy (SEM), and X-ray diffraction (XRD). Additionally, bioactivity studies were conducted using simulated body fluid (SBF), which revealed the formation of apatite during immersion, confirming the material's bioactivity. Vickers microhardness testing demonstrated that Ca-SZ exhibited relatively good hardness, with the highest value recorded at 640.11 ± 31.97 HV for Ca-SZ sintered at 1400°C . These results were comparable to those of a related study that used a commercial zirconia rod (ZrO₂-TZP-A-HIP) as a dental implant, which exhibited a hardness of 804 HV (*Al-Radha et al.*, 2012).

The microhardness of Ca-SZ was found to be influenced by the sintering temperature, with an increase in sintering temperature resulting in increased microhardness. Hussein et al. (2020) supported these statements by conducting Vickers hardness tests, which revealed that Ca-SZ sintered at higher temperatures exhibited greater hardness compared to those sintered at lower temperatures.

Increasing the sintering temperature enhances the density of the material, thereby reducing porosity and minimizing crack formation on the sample's surface. However, in a previous study, it was observed that the relative density of samples sintered at 1600°C decreased to 93% compared to samples sintered at 1450°C , which exhibited a relative density of 94.5%. Excessively high sintering temperatures are not effective in eliminating gas pores (*Chen et al.*, 2009).

Another study also reported that increasing the sintering temperature up to 1450°C was strongly associated with improved material densification. However, further escalation of the temperature led to a rapid decrease in densification due to the surface diffusion process (*Wang et al.*, 2009). Therefore, an optimal sintering

temperature of approximately 1400°C was identified as suitable for achieving optimal densification, considering its positive impact on relative density and porosity.

Despite the promising findings from previous research, mechanical aspects and cell studies were not covered, leaving a gap in the evidence regarding the mechanical properties and biocompatibility of Ca-SZ as dental materials. Therefore, additional mechanical studies involving flexural strength, compression, and fracture toughness are necessary for Ca-SZ research.

Furthermore, biocompatibility testing, including cytotoxicity studies, is essential to ensure that Ca-SZ is non-cytotoxic and safe for use in the oral cavity. This study was carried out to ensure that Ca-SZ mechanical properties were suitable for crown and bridge usage in dental application and biologically safe for implantation by cytotoxicity study to ensure that the materials are non-cytotoxic.

1.3 Justification of Study

The production of zirconia for dental application require incorporating a stabilizing agent to maintain the zirconia phase stability. Addition of CaO as stabilizer help in stabilizing the structure of the zirconia particles as well as enhance the properties of zirconia ceramic. The usage of commercial CaO source can ensure the successful production of stabilized zirconia doped calcia for dental prosthesis application and open up chances for other doping materials to emerge and explore in Malaysian biomaterial industry.

1.4 Scope of Study

The usage of commercial calcium oxide (CaO) as stabilizer was added into zirconia (ZrO₂). A material with suitable mechanical strength, and well dispersed must be achieved to produce Ca-SZ that is suitable to be used as dental material. The surface morphologies of Ca-SZ analysis using Scanning Electron Microscopy (SEM) was performed to ensure a well dispersed material with spherical particles obtained and the material composition as well as crystallinity analysis using X-Ray Diffraction (XRD). The mechanical assessment was carried out to verify that desired characteristics dental implant, crown and bridge material, which is close to the human teeth can be obtained. Mechanical tests conducted were fracture toughness, flexural, and compression test. Thus, the mechanical properties of Ca-SZ obtained was compared with commercial stabilized zirconia, CEREC Zirconia medi S A1, a zirconia block created by Dentsply Sirona Dental System GmbH in Germany, consists of zirconium oxide and is designed for milling blocks. The block is well-suited for applications in crowns and bridges and also has high demand commercially. CEREC Zirconia exhibits excellent biocompatibility and favourable mechanical characteristics suitable for various applications making it suitable as commercial comparison in this study. Cytotoxicity test was conducted as well to ensure safety of the material to be non-toxic.

1.5 Objectives

1.5.1 General Objective

To replicate Ca-SZ, study its cytotoxicity and mechanical properties based on different sintering temperatures.

1.5.2 Specific Objectives

1. To fabricate and characterize calcia stabilized zirconia (Ca-SZ).
2. To investigate the effect of sintering temperature on the compression strength, flexural strength and fracture toughness of Ca-SZ synthesized and compare it with commercial zirconia.
3. To study the cytotoxicity of Ca-SZ cell activity at 1400°C.

1.6 Research questions

1. Is the fabricated Ca-SZ characterized successfully?
2. Is the different sintering temperature affect the compression strength, flexural strength and fracture toughness of Ca-SZ synthesized when compare with commercial zirconia?
3. Does the Ca-SZ cytotoxicity cell activity at 1400°C cytotoxic?

1.7 Research hypotheses

1. The fabricated Ca-SZ is non-cytotoxic to commercial Human Gingival Fibroblast (HGF) cell line.
2. There is significant difference in the mechanical properties of Ca-SZ compared with commercial CEREC Zirconia.

CHAPTER 2

LITERATURE REVIEW

2.1 Biomaterial

Biomaterials study also known as biomaterials science (Tathe *et al.*, 2010). A biomaterial defined as a substance usually utilize and modified for medical applications (Tathe *et al.*, 2010). As reported by (Piehler *et al.*, 2000) that any substance employed to substitute or reinstate the function of human tissue, whether in continuous or intermittent interaction with bodily fluids, can be characterized as a biomaterial. Biomaterial is also known as any substance, whether of natural or synthetic origin, that constitutes a portion or the entirety of a living structure or a biomedical apparatus, serving to replace or imitate a natural function. Bergmann & Stumpf, (2013) agreed with this definition which states that biomaterial is composed of natural or man-made material. It is also stated that biomaterial insertion into the body can improve or maintain the quality of life of the individual.

Williams, (2008) mentioned that the most crucial part of biomaterial is its capability to coexist with human body tissues without inducing any adverse effects to the body. Ige *et al.*, (2012) highlighted that biomaterials consist of elements of biology, medicine, tissue engineering, chemistry and materials science. In general, any man made or natural that serve medical and surgical purposes can be a biomaterial. Biomaterials highly depend on the host response to determine the success rate of its application. The host response (healing) of implanted materials can aid to provide better understanding of biomaterials performance and helps in envisioning

improvement of body response to biomaterials (Ratner and Bryant, 2004). When tissue injured normal healing response is initiated and it can be acute inflammation, granulation tissue formation and also scar formation. For instance, (Ratner & Bryant, 2004) stated that a biomaterial implant named extracellular matrix (ECM) primarily secreted by fibroblasts applied to replace granulation tissue remodelled into scar tissue for wound healing. However, the implants material may cause various reactions known as foreign body reactions (Roach *et al.*, 2007).

Biomaterial can be divided into four primary categories of materials known as, polymers, ceramics, natural materials and metals (Ige *et al.* 2012). Metals usually are synthesized from compound ores such as oxides, sulphides and carbonates except for rare metals like gold and platinum. In ancient times, natural materials have been used as dental materials application (Ige *et al.*, 2012). Natural materials usually do not have any issue with toxicity but have inclination to undergo denaturation or rupture prior to reaching their melting point (Ige *et al.*, 2012). According to Ratner (1996), researchers are inclined towards investigating biomaterials for the replacement of hard tissues (metals and ceramics) in orthopaedic and dental applications, as well as biomaterials for soft tissue replacement (polymers) in cardiovascular and general plastic surgery. Roach *et al.*, (2007) stated that enhancements in biomaterials for applications such as hip replacements and tissue engineering scaffolds have been achieved by advancing alloys derived from metals, polymers, and ceramics. Figure 2.1 shows the total hip replacement design from metal alloy and ceramic.

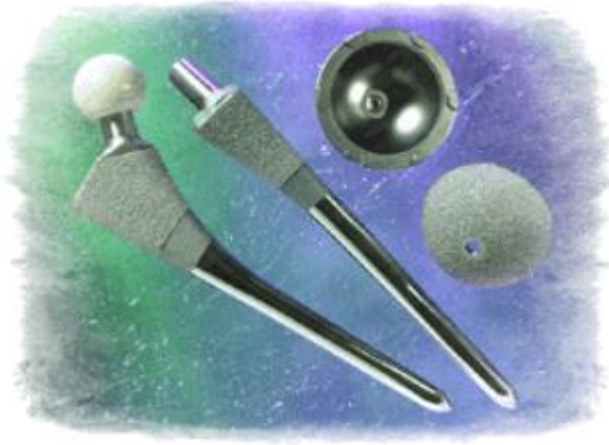


Figure 2.1: Total hip replacement design (Tathe *et al.*, 2010).

A biomaterial is a product widely used in medical application to enhance or replace biological function within the body (Tathe *et al.*, 2010). Usage of biomaterials like hip implant may be bioactive and can last up to 20 years. Meanwhile, (Omidi *et al.*, 2017) mentioned that biomaterials have wide usage of utilization like biosensors and electrodes, tissue engineering, gene therapy, drug delivery, diagnosis of disease, and improvement of healthcare. Orthopaedic implants, prosthetic heart valve, cardiac pacemaker and cardiovascular stents are examples of biomaterial applications in medical field (Piehler *et al.*, 2000).

Lately, biomaterials are actively being used daily in dental application, drug delivery as well as surgery. There is various usage of biomaterials in dentistry such as restorative procedure like dental implants, dentures, dental restoration, surgical procedures, tooth piercings and orthodontics materials. The biomaterials in dentistry may be ceramic (feldspar, zirconia, alumina), metals (titanium and gold) and composites.

Usage of biomaterial product or modification in laboratory may lead to numerous side effects. The occurrence of side effect depends on others factor besides biocompatibility such as processing technique, manufacturing process, sterilization,

modification and place of implantation (Gola, 2019). Therefore, it is a must to conduct biocompatibility test on biomaterial product. The usage of various materials that will be implanted or replaced in human body must have biocompatibility to avoid toxicity in human body system.

2.1.1 Biocompatibility

Biocompatibility has been concerned about implantable device to remain in individual for a long time (Williams, 2008). First generation of implantable device can be traced back to between year 1940 and 1980. It is believed that materials *in vivo* that are known as biocompatible today have been found from the earliest human civilization (Ratner, 2015). Near town Kennewick, Washington remains of male humans found dated over 8000 years ago. The spear point was embedded near pelvis believed to be well healed into bone. There's a strong possibility that the spearhead became encased in a collagenous capsule through a foreign body reaction, similar to how modern medical implants tend to heal while being isolated from the individual's body (Ratner, 2015).

Biocompatibility refers to the material's capacity to interact appropriately with the host's response under specific conditions (Bergmann and Stumpf, 2013). Meanwhile according to Williams (1999), biocompatibility refers to the capability of a biomaterial to fulfill its intended function without causing any systemic effects or undesirable local. Material that successfully implant to human body played important inert roles to body. Williams (2008) stated other terms that normally refer to biocompatibility used widely are non-carcinogenic, non-toxic, non-immunogenic and others. These materials not only insert to perform specific function, but also functions as interface created by introduction of material that generates biological response.

Ratner (2011) believed that most specific favourable cellular or tissue reactions need to be generated in specific situations to optimize the clinically relevant therapeutic outcome as one of the biocompatibility responses. Beyond a material's capacity to provoke the intended biological response, it is more accurate to define it as the interplay between the host, the material, and the anticipated material function (Wataha, 2001). These three factors must be balanced for biocompatible reaction to function properly. Figure 2.2 shows the interaction between these three factors. Wataha (2001) mentioned the interactions between the material, host, and material function persist over time, resulting in an ongoing biological response to the material. The understanding of biocompatibility better through the biochemical, physiological, chemical, physical under specific conditions related with biomaterials contact and body tissue as well as its consequences (Williams, 2008).

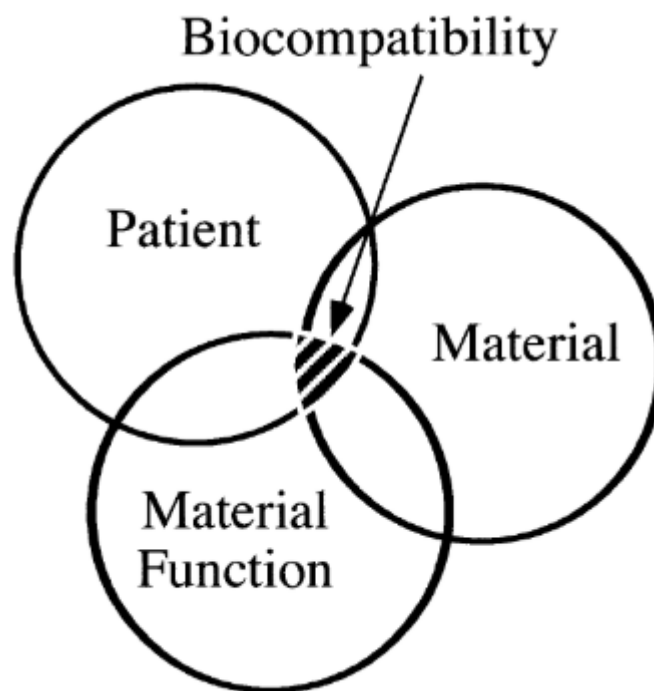


Figure 2.2: Interaction between host, material and material application to generate biocompatibility (Wataha, 2001).

Roach *et al.*, (2007) highlighted that the biocompatibility is influenced by factors such as the implantation site, the implant's function and size, and the duration of its presence which involved time scale interaction between the material and the host. The materials response can vary depending on person and their lifestyle (Williams, 2008). Therefore, risk assessment is crucial to minimize mistake and knowledge gaps in planning biocompatibility test workflow including physicochemical properties and preclinical biological response (Gola, 2019).

There are three types of biocompatibility tests that can be conducted known as *in vitro* test, animal test and usage test (Wataha, 2001). An *in vitro* biological test is conducted within a test tube or culture dish, away from living cells. The bacteria or cells will be in touch with substance. The effect will be determined based on the rate of growth, metabolic responses, or cellular activities of cells in contact with the materials. Animal test uses mammal by placing material inside them. The biological reaction holds more significance than *in vitro* testing, yet controlling the variables can be challenging. Usage test is a clinical test of material. The materials placed within a human participant in its ultimate intended application. This is the most pertinent test for assessing biocompatibility. However, best biological performance is achieved when the device shows least chemical reaction according to Williams (2008).

2.2 Ceramic

According to Fantozzi in 2018, the word ceramics derived from the Greek term "keramikos" (burn soil), brought meaning pottery and clay products which corresponds to the old human activity. The term ceramic is related closely with pottery, brittleness, household and construction (Salamon, 2014). Ceramic is usually known as solid compound which is formed through heat application or both heat and pressure

application that consists of two elements, metal and non-metallic elemental solid (Barsoum, 2002). In simpler words, what is neither polymer, semiconductor nor metal is a ceramic.

This definition is agreed by Retwisch *et al.*, (2011) statement that ceramics are compounds between metallic and non-metallic elements. Meanwhile, Fantozzi (2018) stated a ceramic material is an inorganic substance that lacks metal components and frequently exhibits a crystalline structure. For instance, magnesia (MgO) is classified as a ceramic due to its composition as a solid compound formed by the bonding of a metal with the non-metal oxygen (O₂). (Barsoum, 2002). Oxides, carbides, nitrides, borides and silicides of all metals and non-metallic elemental solids are ceramics.

Atom arrangement in ceramics can be crystalline or amorphous solids. Solids can demonstrate either long-range arrangement, short-range organization, or a combination of the two. Arrangements characterized by extensive order over a significant distance are referred to as crystalline solids, while those lacking periodicity are termed as amorphous, glassy, and non-crystalline solids (Barsoum, 2002). The majority of metals and ceramics possess a crystalline structure, with the exception of glasses and glass ceramics.

Crystalline solids of ceramics exist in two form, single crystals or polycrystalline solids (Barsoum, 2002). Single crystals have repeated arrangement of atoms, periodic and extends without any interference (Salamon, 2014). Polycrystalline structures involve gathering of individual crystals, referred as grains, which are arranged without specific order within regions known as grain boundaries. Grains range from 1 to 50 μm only visible under microscope. Size of grains, shape, presence of porosity and distribution are known as microstructure.

Generally ceramic materials classified to two distinct categories, traditional ceramic and advanced ceramics. Advanced ceramics are widely used in biomaterial and semiconductor product development. One of the ceramics that is currently used widely as biomaterial is zirconia and alumina due to the excellent mechanical properties.

2.2.1 Traditional Ceramic

Conventional ceramics commonly rely on clay and silica as their foundation. (Carter, 2007). Hassan *et al.* (2013), stated that traditional ceramics are constructed from naturally occurring mineral oxides such as silica, alumina, and various other minerals. Then, according to Mason (2016) ceramic materials that arise from readily available, naturally existing raw materials like quartz sand and clay minerals can be defined as traditional ceramic. It was found that traditional ceramic object is nearly as old as the humankind.

Examples of traditional ceramic items encompass fired clay products like tableware, pottery, tiles, and bricks, also cement and alumina. Besides, Abdullah (2014) stated that the solid crystalline compounds have evolved through intricate geological processes over billions of years and are mingled within the Earth's crust. There is also other types of raw materials that are commonly used in traditional ceramic which are kaolinite and feldspar. Conventional ceramics are identified by a porous microstructure based on silicates, which is coarse, non-uniform, and comprises multiple phases. Barsoum (2002) stated typically, they are created by blending clays and feldspars, then shaping through slip casting on a potter's wheel. Subsequently, they undergo sintering in a flame kiln and ultimately receive a glazing process.

2.2.2 Advanced Ceramic

Advanced ceramics refer to the new family of ceramics made of high purity synthetic chemicals (Salamon, 2014). Japanese literature usually called it as ‘fine’ ceramics while in American literature as ‘technical’ or ‘advanced’ ceramic (Matizamhuka, 2018). Barsoum, (2002) also believed that advanced ceramic as a development of advanced raw materials such as carbides, perovskites, binary oxides, and intricate synthetic compounds. This statement was supported by Matizamhuka, (2018) which stated that advanced ceramics have unique properties from other materials such as high hardness, low density, low coefficient of thermal expansion (CTE) as well as higher working temperature.

Salamon, (2014) also added that advanced ceramics are usually categorized according to their composition as oxide or non-oxide ceramics. Advanced ceramics have shown a great performance in its applications including health, electronic appliances, transportation including energy and environment field (Matizamhuka, 2018). It is also notable that the microstructures are finer, less porous and more homogenous (Barsoum, 2002).

Depending on their intended applications, advanced ceramics can be classified into three groups referred to as functional ceramics, nuclear ceramics, and structural ceramics (Salamon, 2014). Structural ceramics are renowned for their exceptional mechanical properties in high temperature and corrosive environment. These ceramics find extensive usage in restorative dentistry as substitute materials, including widely used options like zirconia and alumina. Ceramics with specialized functions are known by their tailor made structures and properties. It is usually used in piezoelectric, dielectric, ferroelectric and thermoelectric. Nuclear ceramics utilize uranium oxide and

nitride for nuclear fuel purposes in the production of ceramic materials. (Salamon, 2014).

2.2.2(a) Sol-gel Technique

Sol-gel chemistry involves the creation of inorganic polymers or ceramics from a solution, progressing from liquid precursors to a sol and eventually forming a network structure known as a 'gel' (Danks *et al.*, 2016). The creation of a sol arises from the hydrolysis and condensation processes of metal alkoxide precursors. Dehghanhadikolaei, (2018) also stated that to obtain 'sol' usually calcium and phosphorus are used followed by addition of two common solvents like distilled water and pure ethanol. In 1974, Flory classified gels into four categories: networks formed from physically aggregated polymers (hydrogels), covalent polymer networks, lamellar gels (involving clays or surfactants), and disordered particle gels. According to Kakihana in 1996, the aim of sol-gel chemistry was to synthesize inorganic solids.

Sol-gel processes originated from the hydrolysis and condensation reactions of metal alkoxides, though they can also occur among hydrated metal species. The majority of alkoxide-based sol-gel instances feature early transition group metals like Ti and Zr, as well as early p-block elements such as Al and Si. Nevertheless, there are numerous cases involving elemental alkoxides as well (Danks *et al.*, 2016). According to Azimi in 2013, sol-gel offers several benefits, including its versatility and capacity to achieve high material purity, the ease of incorporating trace elements, the ability to create unique materials, and energy conservation through low processing temperatures.

2.3 Dental Ceramic

Dental ceramic highlighted three states of its usage according to Kelly & Benetti, (2011). First, to notify professionals that employing ceramics involves the integration of 'high technology' rather than being solely based on 'craft art'. Next, enhance the adaptability of restorative materials and establish a strong foundation in the characteristics of ceramics. 'High technology' concept may refer to the usage of ceramics that modified as dental material for dentist and 'craft art' as a friendly reminder that the materials and techniques borrowed from jewellery making process (Kelly and Benetti, 2011). According to Wang *et al.*, (2013) usage of ceramic as dental restoration materials is influenced by their excellent aesthetics and acceptable mechanical properties, good strength and fracture toughness. In addition, the translucency of ceramics is also one of the crucial factors for ceramic restoration outcomes.

Dental ceramics are also best doppelganger for optical properties of dentin and enamel. Glasses are three-dimensional network (3-D) atoms that do not have regular pattern between nearest neighbour, so they are in amorphous form (Bergmann and Stumpf, 2013). This statement was supported by Robert Kelly (2004) where the glass component in dental ceramics originates from a collection of naturally occurring minerals known as feldspar, which primarily consist of silica and alumina. On top of that, ceramics are applicable for various applications of dental restorations like inlays, onlays, veneers, crown and posts of single-tooth, as well as multi-unit bridge made by stabilized zirconia (Bajraktarova-Valjakova *et al.*, 2018).

A Parisian dentist in 1808, Giuseppangelo Fonzi enhanced the efficacy of ceramics by individually firing denture teeth, each of which contained a platinum pin. This innovation enabled the attachment of teeth to a metal framework involving

reparability, partial denture fabrication and increased aesthetics (Kelly and Benetti, 2011). Introduction of vacuum fired porcelain in early 1960s is also one of the crucial breakthroughs as dental aesthetics. The gold framework was allowed to be concealed by bonded porcelain (McClean *et al.*, 2001). Even the porcelain opaque after firing was later confirmed as initiator for fabrication of ceramic restoration closely resembling a tooth.

Ceramic materials utilized in dentistry commonly rely on silicon, often found in the form of silica (silicon dioxide), owing to silicon's strong affinity for oxygen or as compounds known as silicates (Bajraktarova-Valjakova *et al.*, 2018). According to Robert Kelly (2004) ceramic restoratives can be classified into based on their phases and chemical composition, these materials can be classified into three groups: glass-matrix ceramics, polycrystalline ceramics, and resin-matrix ceramics. Polycrystalline ceramics consist of non-metallic inorganic ceramic materials without a glass phase, while glass-matrix ceramics consist of non-metallic inorganic ceramic materials incorporating a glass phase. Additionally, there are resin-matrix ceramics includes materials of polymer matrix containing inorganic refractory compounds (Bajraktarova-Valjakova *et al.*, 2018).

Crystalline fillers can be mechanically incorporated into the glass by blending glass powders and crystalline materials prior to the firing process. Lately, filler particles have been cultivated within the prosthesis or pellets before being compressed into molds (Kelly, 2004). Heat treatment is applied afterwards causing inducing crystallites expansion and precipitation inside the glass matrix. Example of glass-matrix ceramics are feldspathic ceramic, glass infiltrated ceramic and synthetic ceramic.

The polycrystalline ceramics is a fine-grain crystalline without glass so that the crystals are packed closely together, thus reducing crack propagation and improve the fracture toughness and promote high strength (Bajraktarova-Valjakova *et al.*, 2018). Usage of well-fitting prostheses was facilitated through the utilization of computer-aided manufacturing (CAM) technology (Kelly, 2004). Example of polycrystalline ceramics are zirconia and alumina. Polycrystalline ceramics can be relatively opaque and inadequate for complete wall utilization in aesthetic regions of prosthetics.

Resin matrix ceramic involved in the development of hybrids dental materials comprises an organic matrix densely packed with ceramic particles. The polymer matrix resin displays some characteristics of composite. The materials resist to fracture and are not brittle, and also have shock absorption properties (Bajraktarova-Valjakova *et al.*, 2018). However, this material is only suitable for onlays, inlay and veneers production.

Dental ceramic has evolved greatly with modifications over time for manufacturing processes, packaging, aesthetic properties, chemical composition and indications (Mclaren and Figueira, 2015). Various research has been done to enhance the mechanical characteristics while preserving the material's biocompatibility with the host. CAD/CAM technology also ease the millable and pressable materials for fabrication of ceramic restoration.

2.3.1 Zirconia as Dental Ceramic

Zirconia or named as metal zirconium, came from Arabic Zargon (golden colour) originates from the fusion of two Persian terms, "Zar" meaning gold, and "Gun" meaning colour (Piconi *et al.*, 1997). German chemist Martin Heinrich Klaproth initially discovered metal dioxide zirconia (ZrO_2) in the year 1789 (Mughtar *et al.*,

2012). Zirconium (Zr) is a comparatively lustrous silvery metal that displays softness and flexibility in its highly pure state (Bajraktarova-Valjakova *et al.*, 2018). Zirconia constitutes approximately 0.02% of the Earth's crust, with the primary deposits found in South Africa and Brazil as monolithic zirconia, while significant proportions are present in India and Australia in the form of zircon ($ZrSiO_4$) sand.

The exceptional mechanical properties of zirconia distinguish it as a prominent member among oxide ceramics (Denry and Kelly, 2008). Zirconia, which is the dioxide of zirconium, is characterized by three distinct crystal structures referred to as monoclinic (M), tetragonal (T), and cubic (C). At room temperature, pure zirconia exists in the monoclinic phase, it transformed to tetragonal phase as temperature elevates up to 1170°C and cubic phase at 2370°C (Mughtar *et al.*, 2012). Bajraktarova-Valjakova *et al.*, (2018) this situation is referred to as allotropy, as it involves various structures with comparable chemical compositions but differing atomic arrangements.

The zirconia lattice parameters are shown in Table 2.1. The cubic phase is characterized by a sole lattice constant, denoted as ' a '. The Zr atoms are positioned within a face-centered cubic (fcc) arrangement, while the O atoms are regarded as moving within tetrahedral interstitial sites linked to the fcc arrangement. Tetragonal phase can be visualized as a deformation of the cubic structure. All parameters can be examined along the a -, b -, and c -directions in the monoclinic phase. This phase possesses lattice parameters a , b , and c , along with an orthogonal angle between the a and c axes.

Table 2.1 Lattice parameters of zirconia at room temperature (Hannink *et al.*, 2000).

	Structures	a (Å)	b (Å)	c (Å)	β	q_{Zr}	q_{Si}	q_o
Zirconia	Cubic	5.12	5.12	5.12	90°	2.4	2.4	-1.2
	Monoclinic	5.19	5.25	5.29	99.23°			
	Tetragonal	6.56	6.56	6.14	90°			

According to Kelly & Benetti (2011) ceramics engineer in the late 1980s realized that addition of small amounts of metal oxides (3-8 mass %) can stabilize tetragonal phase at room temperature. Incorporation of stabilizing metal oxides including magnesium oxide (MgO), calcium oxide (CaO), cerium oxide (CeO₂) and yttrium oxide (Y₂O₃), allow metastable state of zirconia and stop crack propagation which lead to high toughness (Denry and Kelly, 2008). However, the sandblasting and grinding for surface treatments might trigger the t→m transformation by expanding in volume, resulting in the creation surface compressive stress. It can increase flexural strength, but alteration phase of material may lead the possibility to aging faster (Denry and Kelly, 2008).

The prostheses of zirconia as dental ceramic almost lifelike despite the opaque structure (Kelly and Benetti, 2011). Fracture toughness of zirconia is twice the alumina which makes it an interesting substructure material (Kelly and Benetti, 2011). Three common types of zirconia employed in dental restoration applications include yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP), magnesium partially stabilized zirconia (Mg-PSZ) and zirconia-toughened alumina (ZTA).

2.3.1(a) Magnesium Partially Stabilized Zirconia (Mg-PSZ)

Reportedly, Mg-PSZ is considered inappropriate for dental applications due to the large grain size and high porosity which can initiate large crack propagation and surface wear (Gautam *et al.*, 2016). This assertion also backed by Amat *et al.*, (2012)

and Abd El-Ghany & Sherief, (2016) that mentioned that the large grain size varying from 30-60 μm can cause surface wear due to low stability of materials. Denry & Kelly (2008) also stated the amount of MgO in the composition relatively high, ranging between 8-10 mol %.

Besides that, Mg-PSZ has higher sintering temperature (1680-1800°C) compared to other zirconia stabilized metal oxide causing the cooling cycle to be controlled strictly (Denry and Kelly, 2008). Piconi & Maccauro (1997) and Abd El-Ghany & Sherief (2016) also agreed with the statement and added that the strict control required close attention in ageing step that usually occur around 1100°C during t-phase precipitation. During this phase, the precipitation of the transformable t-phase can take place, making the volume fraction a critical factor in regulating the material's fracture toughness (Abd El-Ghany and Sherief, 2016).

The poor stability of Mg-PSZ could potentially result in a slightly reduced energy requirement for the transformation from tetragonal to monoclinic phase. Additionally, acquiring free silica, which is a precursor for Mg-PSZ (SiO_2), can be challenging. The presence of magnesium silicate can reduce the quantity of magnesia, which promotes the transformation from tetragonal to monoclinic phase hence lowering the mechanical properties and stability of materials (Abd El-Ghany and Sherief, 2016). Piconi & Maccauro (1997) believed that the SiO_2 contents increase due to the wear of milling media during powder processing before firing takes place.

2.3.1(b) Zirconia Toughened Alumina (ZTA)

ZTA is the combination of zirconia and alumina matrix and is reported to have high resistance to crack propagation, thus improving its function as a lifetime reliability for joint prostheses (Gautam *et al.*, 2016). This statement is also substantiated by Madfa *et al.*, (2014) stated a higher threshold for the stress intensity

factor does not prevent crack propagation from occurring. In addition, the tetragonal phase stability does not require any usage of doping and is instead controlled by morphology, particle size, and grain size (Gautam *et al.*, 2016). Abd El-Ghany & Sherief, (2016) study also stated that even though there is only 10% in volume of zirconia, that is relatively low, but they show similar hardness value to other substances such as aluminum oxide (Al_2O_3) are also resistant to hydrothermal instability.

One of the commercial dental products available is In-Ceram Zirconia (VidentTM, Brea, CA) was created by introducing 33 vol % of 12 mol% ceria-stabilized zirconia (12 Ce-TZP) into In-Ceram alumina (Abd El-Ghany and Sherief, 2016). In-Ceram zirconia can undergo processing using methods like slip casting or soft machining. Optimal sintering conditions were observed at 1100°C for a duration of two hours. However, it is highly recommended to use slip casting technique due to the limited shrinkage effect (Madfa *et al.*, 2014).

2.3.1(c) Yttria Stabilized Tetragonal Zirconia Polycrystal (3Y-TZP)

Since the late eighties biomedical grade zirconia is manufactured with a stabilizer consisting of 3 mol % yttria (Y_2O_3) (Abd El-Ghany and Sherief, 2016). This statement is supported by Bajraktarova-Valjakova *et al.*, (2018) and Lazar *et al.*, (2008) that also added the addition of 3 mol % yttria related to the transformation for monoclinic phase when a mechanical stress is applied. This modification can inhibit crack propagation and enhance the material's toughness and mechanical strength (Lazar *et al.*, 2008).

Y-TZP has high biocompatibility compared to other stabilized ceramics (Alfawaz, 2016). Tetragonal grains of 3Y-TZP are thermodynamically unstable below 700°C and may transform into monoclinic phase under externally applied stress like