SYNTHESIS OF NANO CALCIUM OXIDE FROM COCKLE SHELLS AS STABILIZER FOR FABRICATION OF ZIRCONIA

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by

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LIST OF ABBREVIATIONS

BET	Brunaur-Emmett-Teller surface area analysis
CaO	Calcium oxide
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
CNB	Chevron- notched beam
DDW	Double distilled water
EDX	Energy Dispersive X-ray
FDPS	Fixed partial dental prostheses
HCl	Hydrochloric acid
Hv	Vickers' hardness
IF	Indentation fracture
IS	Indentation strength
K_2CO_3	Potassium carbonate
LTAD	Low-temperature aging degradation
LTD	Low temperature-degradation
Mg-PST	Magnesium partially- stabilized zirconia
PSZ	Partially stabilized zirconia
PTT	Phase transformation toughening
SEM	Scanning electron microscope
SENB	Single -edge notched beam
SCF	Surface crack in flexure
TGA	Thermogravimetric analyzer
XRD	X-ray diffractometer

XRF	X-Ray Fluorescence
Y-TZP	Yttria-stabilized tetragonal zirconia polycrystals
ZrO_2	Zirconium dioxide
ZTA	Zirconia- toughened alumina

SINTESIS NANO KALSIUM OKSIDA DARIPADA KULIT KERANG SEBAGAI PENSTABILAN UNTUK PEREKAAN ZIRKONIA

ABSTRAK

Pelbagai kajian mencadangkan bahawa kulit kerang mempunyai potensi yang besar sebagai sumber kalsium oksida semula jadi (CaO). Oksida yang berbeza telah digunakan untuk menstabilkan zirkonium oksida (ZrO_2) dalam fasa yang stabil. Penggunaan CaO sebagai penstabil telah dikaji sebelum ini; walau bagaimanapun, CaO disediakan secara komersil telah digunakan untuk tujuan ini. Tujuan kajian ini adalah untuk mendapatkan CaO dari sisa kulit kerang dan menggunakannya untuk menstabilkan ZrO_2 dan kemudian membandingkannya dengan ZrO_2 yang distabilkan dengan CaO komersial. Sifa*t*-sifat fizikal dan mekanik dari zodiak CaO yang terbentuk dari kedua-dua sumber juga dikaji. Sampel $CaCO_3$ dan CaO dicirikan dengan menggunakan pengimbasan mikroskop elektron, analisis kawasan permukaan Brunaur-Emmet*t*-Teller, analisis difraksi sinar-X dan analisis sinar-dispersif tenaga. CaO diperolehi melalui proses penalaan pada suhu 300-750℃. Morfologi $CaCO_3$ dikawal oleh manipulasi parameter tindak balas seperti kepekatan DDW, kadar penambahan K_2CO_3, dan kepekatan pelarut organik. Kalsium oksida digunakan untuk menstabilkan sintering zirkonium (A) 9.2 g zirkonium oksida yang dibeli secara komersial dicampurkan dengan 0.8 g kalsium oksida yang diperolehi daripada kulit kerang. (B) 9.2 g zirkonium oksida yang dibeli secara komersial dicampurkan dengan 0.8 g kalsium oksida yang dibeli secara komersial. Setiap campuran spesimen ditekan dalam acuan keluli tahan karat menggunakan tekanan hidrolik di bawah tekanan 5 tan (60MPa) tekanan dan disinter untuk pelbagai masa (satu, dua, tiga, dan empat jam) pada suhu yang berbeza (1200 °C, 1300 °C, 1400 °C, and 1500 °C) untuk menghasilkan pelet zirkonia yang distabilkan dengan CaO. Pencirian SEM zirconia stabil dengan menggunakan kulit kerang mempunyai saiz zarah purata 61.13 nm dibandingkan dengan zirkonia stabil dengan menggunakan nano CaO komersial yang mempunyai ukuran zarah rata-rata 64.37 nm. Nanopartikel yang dihasilkan berbentuk bulat dan tersebar sama rata tanpa aglomerasi. Analisis komposisi EDX menunjukkan bahawa peratusan zirkonia lebih tinggi di dalam zirconia yang distabilkan dengan nano CaO dari kulit kerang berbanding kormesial. Analisis XRD mendedahkan bahawa puncak tertinggi bagi nano CaO kristal zirkonia yang stabil dicatatkan pada sudut $2\theta = 30°$ yang menggambarkan kristal zirconia berbentuk sfera.Ujian kekuatan fleksural, ujian kekuatan mampatan, ujian kekerasan Vickers dan ujian ketumpatan dilakukan bagi setiap sampel. Ujian ini menyimpulkan bahawa zirkonia yang distabilkan dengan nano CaO dari kulit kerang mempunyai sifat mekanikal dan fizikal yang unggul dan setanding dengan zirconia yong distabilkan dergan kormesial nano CaO apabila disinter pada 1400 ° C selama 2 jam . Dapat disimpulkan dari kajian kami bahawa kulit kerang adalah sumber nano CaO yang baik. Ujian mekanikal dan fizikal membuktikan bahawa zirconia yang distabilkan dengan nano CaO yang diambil dari kalit kerang dianggap sesuai untuk aplikasi pergigian.

SYNTHESIS OF NANO CALCIUM OXIDE FROM COCKLE SHELLS AS STABILIZER FOR FABRICATION OF ZIRCONIA

ABSTRACT

Various studies suggest that cockle shells hold great potential as a rich source of natural calcium oxide (CaO). Different oxides have been used to stabilize zirconium oxide (ZrO_2) in a stable phase. Use of CaO as a stabilizer has been studied previously; however, commercially prepared CaO has been utilized for these purposes. The aim of the current study was to derive CaO from cockle shell waste and to utilize cockle shell derived CaO for stabilizing ZrO_2 and then to compare it with ZrO_2 stabilized with commercial CaO. The physical and mechanical properties of the CaO stabilized zirconia derived from both sources were also investigated. $CaCO_3$ samples were characterized using scanning electron microscopy, Brunaur-Emmett-Teller surface area analysis, X-ray diffraction analysis and energy dispersive X-ray analysis. The CaO was obtained through calcination process at a temperature range from 300-750 °C. The morphology of $CaCO_3$ were controlled by manipulation of reaction parameters such as DDW concentration, K_2CO_3 feeding rate, concentration of organic solvents, and the drying methods. The calcium oxide was used to stabilize zirconium sintering. (A) 9.2 g of commercially purchased zirconium oxide was mixed with 0.8 g of calcium oxide derived from cockle shells. (B) 9.2 g of commercially purchased zirconium oxide was mixed with 0.8 g of calcium oxide which was commercially purchased. Each specimen mixture was pressed in stainless steel mold using hydraulic press under 5 tons (60MPa) pressure and sintered for various times (one, two, three, and four hours) at different temperatures (1200 °C, 1300 °C, 1400 °C, and 1500 °C) to fabricate pellets/blanks of CaO stabilized zirconia. SEM characterization of zirconia stabilized using cockle shells had an average particle size of 61.13 nm as compared to zirconia stabilized using commercial CaO that had an average particle size of 64.37 nm. It was noted that the nanoparticles had spherical shape and they were evenly distributed with no visible agglomeration. EDX composition analysis revealed that percentage of zirconia was higher in zirconia stabilized using nano CaO derived from cockle shells in comparison to zirconia stabilized using commercial nano CaO. XRD analysis revealed that the highest peak for the nano CaO stabilized zirconia crystals in the XRD pattern was noted at an angle $2\theta=30°$ depicting spherical crystals of zirconia. Flexural strength test, compressive strength test, Vickers hardness test and density test were performed for each sample. These tests concluded that nano CaO stabilized zirconia from cockle shell is comparable to zirconia stabilized by commercial nano CaO and had superior mechanical and physical properties when sintered at 1400 °C for 2 hours holding time. It can be concluded from our study that the cockle shell waste is a rich source of nano CaO. Mechanical and physical tests prove that nano CaO stabilized zirconia derived from cockle shell can be considered suitable for dental applications.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Zirconia, also known as zirconium dioxide (ZrO_2) is a white crystalline oxide of zirconium. It is a super hard material owing to its peculiar arrangements of atoms (Hambire and Tripathi, 2013). Mineral baddeleyite with a monoclinic crystalline structure is its most naturally occurring form. The name zirconium, comes from the Arabic Zargon (golden in colour), which in turn comes from the two Persian words Zar (Gold) and Gun (Colour).

Zirconia occurs as a monoclinic, cubic or tetragonal polymorph. Only the monoclinic phase ZrO_2 exists at room temperature, which is stable up to 1170 °C when it inverts to a tetragonal, metastable phase. At above 2370 °C the zirconia turns into a cubic (Živko-Babić *et al.*, 2005). The research on the use of zirconia ceramics as biomaterials started about forty years ago (Stilwell and Tabor, 1961). Due to its excellent mechanical properties, zirconia holds a unique place amongst oxide ceramics (Piconi and Maccauro, 1999).

In combination with CAD/CAM (Computer Aided Design/computer Aided Manufacturing) techniques, zirconia has been recently introduced in prosthetic dentistry for the fabrication of crowns and fixed partial dentures (Denry and Kelly, 2008). By the addition of stabilizing oxides such as calcium oxide (CaO), magnesium oxide (MgO), ceria (CeO_2), alumina (Al_2O_3) or Yttria (Y_2O_3) to pure zirconium dioxide, a multiphase material is obtained, known as partially stabilized zirconia (PSZ)

(Živko-Babić *et al.*, 2005). The three zirconia-containing ceramic systems used to date in dentistry are yttrium cation-doped tetragonal zirconia polycrystals (3Y-TZP), magnesium cation-doped partially stabilized zirconia (Mg-PSZ) and zirconia-toughened alumina (ZTA) (Denry and Kelly, 2008). Until recently, yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) has been commonly used to produce dental prosthetic infrastructures, due to its excellent mechanical properties corresponding to a high flexural strength (up to 900–1200 MPa) and high fracture toughness (5.9– 10 MPa $m^{½}$) highest ever reported for any dental ceramic (Santos *et al.*, 2016).

A cockle is a small, edible, saltwater clam, a marine bivalve mollusc that lives in sandy, sheltered beaches throughout the world. In the South East Asian region, including Malaysia, cockles (Anadara granosa) are an important source of protein (Awang-Hazmi *et al.*, 2007). Cockles are abundant in Malaysia and are called ‘kerang’ in Malay.

The shell of the cockle known as the cockle shell is a rich source of calcium carbonate ($CaCO_3$), along with trace amounts of other materials including silicon dioxide, sodium oxide, and aluminium oxide (Muthusamy *et al.*, 2016).

Once the cockles have been extracted for human consumption, the shells have no commercial value. In 2007, the estimated retail value of cockles alone was over 32 million US dollars (Department of Fisheries Malaysia, 2008). The consumption of such large quantities of cockles leaves behind a generation of abundant waste shells which can be used for industrial applications. Although cockle shells are considered as biomass waste, recently there have been several efforts to utilize them for commercial purposes (Buasri *et al.*, 2013).

The composition of CaO in cockle shells is higher compared to other naturally occurring sources such as limestone. Findings from comparative studies on scallop shells, (Buasri *et al.*, 2013)sea shells and crab crust and legs on the composition of calcium-based compound in marine shells justifies the use of cockle shells as a more potential biomass for calcium oxide (Jeon and Yeom, 2009; Li *et al.*, 2009).

1.2 Problem statement

Growing need for metal-free and aesthetically pleasing restorations have promoted the development of high strength ceramic crown and bridge systems. In lieu of its strength and aesthetic properties, zirconia (ZrO_2) is a suitable substructure for crown and bridge systems (Burke *et al.*, 2013). For industrial applications; pure zirconia is of limited use due to the phase transformations that occur. The phase transformation results in a volumetric change which is not suitable for equipment requiring precise measurements of sintered structures.

To overcome this problem, zirconia can be blended with certain oxides to reduce the impact of stresses which lead to crack propagation consequently to cooling down from elevated temperatures.

Yttrium stabilized and ceria-stabilized zirconia has the disadvantage of inferior machining associated with wear of the tool due to the superior hardness of those materials. Partially sintered Y-TZP produces extensive sintering shrinkage during the pos*t*-sintering process which might affect the final fit of the zirconia framework. Y-TZP also suffers from low-temperature aging degradation (LTAD) caused by phase transformation. Therefore, partially and fully stabilized zirconia using nano-CaO can serve as a suitable replacement.

Countless efforts have been made to stabilize zirconia with calcium oxide. However, in all cases, the particles size of stabilizers was not clearly described (Kelly and Denry, 2008). Moreover, the use of nano-CaO to stabilize zirconia for dental application has not been reported. In this project, nano-CaO derived from cockle shell for dental application will be used to stabilize zirconia. Cockle shell derived CaO nanoparticles could yield a better microstructure of stabilized zirconia with good material properties, as often obtained by the commercial calcium oxide. Cockle shells are natural sources of calcium oxide and readily available as waste. Calcium oxide is biocompatible and is one of the compositions of hydroxyapatite in human bone. Therefore, using nano-CaO from cockle shell not only benefits the waste removal (recycling) but also adds economic value to these sea shells.

The cockle shell is an excellent source of calcium oxide and is abundantly available in Malaysia. To date, a few studies have used various sea shells as a primary source of

CaO. Crab shells, eggs shells, oysters and other shells have been previously used as an alternative source of natural CaO (Mohamed *et al.*, 2012). Moreover, the use of calcium oxide derived from cockle shells to stabilize zirconia for dental applications has not been reported. Therefore, in the current study, cockle shells will be used to obtain CaO as a stabilizer for zirconia for dental application, as they are a natural source of CaO and readily available as biomass waste.

1.3 Justification of the study

Calcium oxide, which is an oxide used to stabilize zirconia is a major component of the cockle shell. Malaysia has an abundant cockle shell waste and utilization of this waste to produce CaO holds immense potential. The fabrication of zirconia stabilized with CaO derived from cockle shell with properties comparable to zirconia stabilized with commercial CaO will enable the production and commercialization of a new dental prosthetic material using biomass waste which will add one more commercial product for the Malaysian industry.

1.4 Scope of the study

Concerns regarding the biocompatibility limitations and optical and aesthetic shortcomings of metal-ceramic restorations have ignited a shift to all-ceramic prosthodontics. There is also a growing popularity and demand for ceramic prosthodontic appliances as the general population is becoming more aware of the options available for their dental need. This demand opens opportunities for exploration of newer value added dental restorative materials. The availability of abundant supply of cockle shells allows its use as a source of calcium oxide for use as stabilizer in zirconia based dental ceramic material.

Malaysia is dependent on imported dental ceramic materials from other countries to serve its population. The development of a newer dental ceramic material using a biomass waste as a source of stabilizer will aid in the possible commercialization of the product and add value to the cockle shell biomass waste, which usually ends up as landfill.

1.5 Objectives

General objectives

To fabricate zirconia stabilized with nano CaO derived from cockle shells and commercial nano CaO.

Specific objectives

1. To synthesize and characterize nano $CaCO_3$ derived from cockle shells and determine the optimal conditions for its synthesis.
2. To synthesize CaO from $CaCO_3$ precursor obtained from objective one by calcination process and to characterize synthesized CaO using scanning electron microscope (SEM).
3. To fabricate zirconia stabilized by nano CaO derived from cockle shells, and zirconia stabilized by commercial nano CaO using ball milling technique and sintered at different temperatures.

4. To compare the characteristics of zirconia stabilized by nano CaO derived from cockle shells and zirconia stabilized by commercial nano CaO sintered at different temperatures.
5. To compare the physical and mechanical properties zirconia stabilized by nano CaO derived from cockle shells and zirconia stabilized by commercial nano CaO sintered at different temperature.

1.6 Research question

1. Is it possible to synthesize and characterize nano $CaCO_3$ derived from cockle shells and what are the optimal conditions for its synthesis?
2. Is it possible to synthesize CaO from $CaCO_3$ precursor from objective one by calcination process and what are the characteristics of synthesized CaO using scanning electron microscope (SEM)?
3. Is it possible to fabricate zirconia stabilized by nano CaO derived from cockle shells and zirconia stabilized by commercial nano CaO using ball milling technique and sintered at different temperatures?
4. Is there any significant difference between the characteristics of zirconia stabilized by nano CaO derived from cockle shells, and zirconia stabilized by commercial nano CaO sintered at different temperatures?
5. Is there any significant difference between the physical and mechanical properties of zirconia stabilized by nano CaO derived from cockle shells, and zirconia stabilized by commercial nano CaO sintered at different temperature?

1.7 Research hypotheses

1. It is possible to synthesize and characterize nano $CaCO_3$ derived from cockle shells.
2. It is possible to synthesize and characterize nano CaO from $CaCO_3$ precursor from objective one by calcination process.
3. It is possible to fabricate zirconia stabilized by nano CaO derived from cockle shells, and zirconia stabilized by commercial nano CaO using ball milling technique and sintered at different temperatures.
4. There is a significant difference between the characteristics of zirconia stabilized by nano CaO derived from cockle shells, and zirconia stabilized by commercial nano CaO sintered at different temperatures.
5. There is a significant difference between the physical and mechanical of properties zirconia stabilized by nano CaO derived from cockle shells, and zirconia stabilized by commercial nano CaO sintered at different temperature.

CHAPTER TWO

LITERATURE REVIEW

2.1 Zirconia

Zirconium was discovered in 1789 in Berlin (Germany) as a product of gem heating reaction by Martin Heinrich Klaproth. However, it was isolated by Jons Jacob Berzelius, a Swedish chemist in the year 1824 (Hisbergues *et al.*, 2009). Zirconia, also known as zirconium-dioxide (ZrO_2), is a white mineral.

Pure zirconia has three polymorphic phases at room temperature and pressure as displayed in the Figure 2. 1. The monoclinic phase is stable up to 1170 °C. While tetragonal phase exists from 1170 to 2370 °C and cubic phase is formed at temperatures above 2370 °C (Goff *et al.*, 1999; Kelly and Denry, 2008). Upon cooling, the volume changes links to these phase transformations can destabilize the chemical structure making it unsuitable for technical applications.

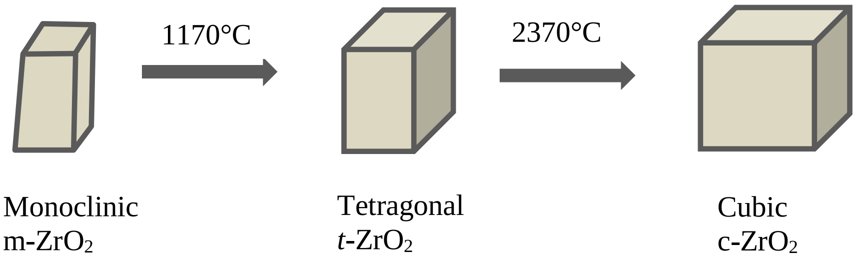

Figure 2. 1 Polymorphic phases of zirconia (Adapted from Goff and colleagues (1999) and Kelly and Denry (2008))

Advances in strengthening bio ceramics have been made over decades using several techniques. However, further improvements are needed because mechanical failure is still the limiting factor of their lifetime (Denry and Kelly, 2008; Kelly and Denry, 2008). Laser interference direct structuring has been proven to scale and improve mechanical properties. It has been shown that this technology can periodically treat and control grain sizes and pore structures on the surface of zirconia without chemically changing the material or introducing phase transformations (Noushad and Noushad, 2009).

With the aim of replacing the infrastructure of metallic dental prosthetic, structural ceramics have been improved and have become increasingly more popular in dentistry. Among the dental ceramics, zirconia has emerged as a versatile and promising material because of its biological, mechanical and optical properties, which has certainly accelerated its routine use in CAD/CAM technology for different types of prosthetic (Hamza *et al.*, 2013).

Zirconia based ceramics are routinely used in structural applications in engineering, such as in the manufacture of cutting tools, gas sensors, refractoriness and structural opacifiers (Rashad and Baioumy, 2008). To meet structural demands, zirconia is doped with stabilizers to achieve high strength and fracture toughness (Kelly and Denry, 2008). The bio ceramics that are currently used in medical and dental care are derived from structural materials used in aerospace and military arms or, which were modified to suit the additional requirements of biocompatibility (Thompson *et al.*, 2007; Vagkopoulou *et al.*, 2009).

2.2 Phase transformation

At ambient pressure, unalloyed zirconia can be found in three crystallographic forms depending on the temperature. At room temperature and upon heating up to 1170 °C, it is monoclinic (m). At temperature between 1170 °C and 2370 °C it is tetragonal (t) and above 2370 °C and up to the melting point it is cubic (c). Upon cooling, the transformation from the tetragonal (t) phase to the monoclinic (m) phase is characterized by a substantial increase in volume (about 4.5%), sufficient to lead to catastrophic failure. This transformation begins at 950ºC and is reversible (Chevalier *et al.*, 2004). (Garvie *et al.*, 1975) in their important paper “Ceramic Steel” showed the best method to use phase transformation of zirconia to improve the mechanical strength and toughness of this type of ceramics. They stated that tetragonal phase precipitates that are finely dispersed within the cubic matrix were able to be transformed into the monoclinic phase when the constraint exerted on them by the matrix was relieved by a crack propagated within the matrix. The stresses resulted from this phase transformation into a larger size phase will act in opposite direction to the stress fields that initiate and promotes crack propagation. Such mechanism will result in enhancement in fracture toughness as the energy associated with crack propagation is dissipated in both phase transformation and in overcoming stresses due to the volume expansion. This process is known as transformation toughening (Garvie and Nicholson, 1972). It was discovered that such strong ceramic could result from alloying of pure zirconia with lower valance oxides, such as MgO, La_2O_3, CaO and Y_2O_3, and this decreased the amount of strained m phase at room temperature and favoured more symmetric c and t lattice structures. These c and t phases are analogous to those in pure zirconia but have dopant ions substituted on Zr^{4+} sites and have a fraction of oxygen sites vacant to retain charge neutrality (Chevalier *et al.*, 2004). Different types of zirconia ceramics materials are available for dental applications. Various processing routes and synthesis methods used to obtain ZrO_2 powders have been tabulated in Table 2.1.

Table 2. 1 Processing route and synthesis method used to obtain ZrO_2 powders (Sōmiya and Akiba, 1999)

Processing route	**Synthesis method**
1. Thermal decomposition	a. Heating (evaporation) b. Spray drying c. Flame spraying d. Plasma spraying e. Vapor phase (CVD) f. Freeze drying g. Hot kerosene drying h. Hot petroleum drying
2. Precipitation or hydrolysis	a. Neutralization and precipitation b. Homogeneous precipitation c. Coprecipitation d. Salts solution e. Alkoxides f. Sol-gel
3. Hydrothermal	a. Precipitation (coprecipitation) b. Crystallization c. Decomposition d. Oxidation e. Synthesis f. Electrochemical g. Mechanochemical h. RESA (reactive submerged arc) i. Hydrothermal + microwave j. Hydrothermal + Ultrasonic
4. Melting and rapid quenching	

2.3 Phases of zirconia (monoclinic, tetragonal and cubic)

The spatial arrangement of the atoms in zirconia is characterized by distinct crystallographic structures, characterizing a property known as polymorphism. Its three phases, or crystal structures, are characterized by specific geometry and dimensional parameters: monoclinic, tetragonal and cubic (Figure 2. 2 a, b, c). Pure zirconia has a monoclinic structure at room temperature, which is stable up to 1170 °C. Between this temperature and 2370 °C, tetragonal zirconia is formed, while cubic zirconia is formed at temperatures above 2370 °C. After processing, and depending on the cooling process, the tetragonal phase becomes monoclinic at about 970 °C. Due to polymorphism, pure zirconia cannot be used at elevated temperatures due to a large volume change (3-5%) which occurs during cooling to the monoclinic phase. This change is sufficient to exceed the elastic and fracture limits, resulting in cracks and flaws in ceramics (Denry and Kelly, 2008).The transformation of the tetragonal to monoclinic phases can be employed to improve the mechanical properties of zirconia, especially its tenacity. The mechanism involved is known as a booster from transformation. This transformation is martensitic in nature; therefore, a process that occurs by shear without diffusion, i.e. the atomic position change occurs abruptly at a speed close to the speed of sound propagation in solids. The reverse transition, i.e. the monoclinic > tetragonal transformation and occurs at approximately 1170° C, while the tetragonal > monoclinic transformation, which occurs during cooling, is observed between 850 and 1000 °C, depending on the strain energy. Therefore, the manufacturing of components of pure zirconia is not possible due to spontaneous failure. The addition of stabilizing oxides is important because it allows the maintenance of the tetragonal form at room temperature (Hannink *et al.*, 2000). Different oxides, such as yttrium oxide (Y_2O_3), calcium oxide (CaO) or magnesium oxide (MgO), can be added to zirconia to stabilize it, allowing the tetragonal form to exist at room temperature after sintering. The addition of varying amounts of stabilizers allows the formation of partially or fully stabilized zirconia which, when combined with changes in processes, may result in ceramics with exceptional properties such as high flexural strength and fracture toughness, high hardness, excellent chemical resistance and good conductivity ions. A fully stabilized zirconia is obtained by adding sufficient amounts of stabilizing oxides, such as 16mol% magnesia (MgO), 16mol% of limestone (CaO) or 8 mol% yttria (Y_2O_3). Since the partial stabilization of zirconia is obtained with the same oxides, but in smaller amounts (e.g. 2 mol% to 3mol% yttria), a multiphase structure is created, which usually consists of tetragonal and cubic zirconia majority monoclinic precipitated in small amounts(Piconi and Maccauro, 1999). The transformation of tetragonal zirconia into monoclinic is a phenomenon influenced by temperature, vapour, particle size, micro-and macrostructure of the material, and also by the concentration of stabilizing oxides. The critical particle size for the partially stabilized zirconia to be maintained in the tetragonal form at room temperature is 0.2µm to 1µm (for compositions ranging from 2% to 3 mol% yttria), because, under 0.2 µm, the transformation to the monoclinic phase is not possible (Kelly and Denry, 2008)

2.3.1 Monoclinic zirconia

The natural form of zirconia, known as baddeleyite, contains approximately 2% HfO_2 (hafnium oxide), which is very similar to zirconia in structure and chemical properties. Zr^{4+} ions have a coordination number of seven for the interstices, with the average distance between the zirconia ion and three of the seven oxygen ions is 2.07Å. Since the average distance between the zirconium ion and four oxygen ions is 2.21Å, in the structure, one of the angles (134.3°) differs significantly from the tetrahedral value (109.5°). Thus, the structure of the oxygen ion is not planar and a curve occurs in the plane of the four oxygens, and the plane of three oxygens is completely erratic (Hannink *et al.,* 2000).

2.3.2 Tetragonal zirconia

Zirconia in its tetragonal phase has the form of a straight prism with rectangular sides. Ions Zr^{4+} have a coordination number of eight, where the shape once again appears distorted due to the fact that four oxygen ions are at a distance of 2.065Å in the form of a tetrahedron plan, and four others are at a distance of 2.455Å in a tetrahedron that is elongated and rotated 90° (Vagkopoulou *et al.*, 2009).

2.3.3 Cubic zirconia

The structure of cubic zirconia can be represented by a simple cubic lattice with eight oxygen ions, which are surrounded by a cubic arrangement of cations, known as fluorite, i.e. the oxygens occupy the tetrahedral interstices of a cubic lattice (CFC) of cations (Vagkopoulou *et al.*, 2009).

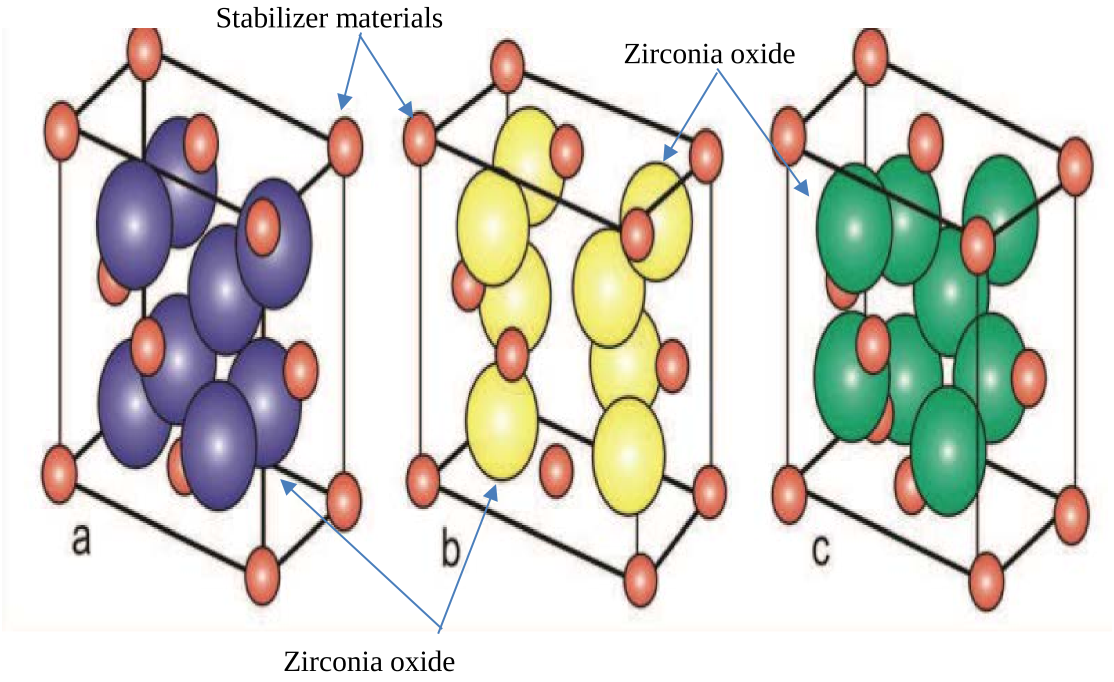

Figure 2. 2 Crystal structure of monoclinic (a), tetragonal (b) and cubic zirconia(c) (Hannink *et al.*, 2000)

2.4 Martensitic transformation

The characteristic of phase transformations that zirconia suffers is of the martensite type. The term ‘martensite’ is a phenomenon which is used to described the microstructure of a hardened steel (Kelly and Rose, 2002). In metallurgy, this process is characterized by a transformation that takes place without mass transfer, in ascertain range of temperatures and changes the shape of the nucleus. Phase transformations are reversible, and involve the expansion of the core volume by approximately 3 to 4 %.With the stabilization of zirconia by oxides (CaO, MgO, Y_2O_3, CeO_2 or other rare earths), tetragonal and cubic phases may be partially or fully stabilized, allowing the determination of mechanical properties necessary for their use (Tsalouchou *et al.*, 2008). The transformation is thermodynamically reversible to 1174 °C and the change in atomic position shows a curve of thermal hysteresis between heating and cooling cycles. The intensity of the martensitic transformation is influenced by several parameters, such as size, shape and location of the particles of ZrO_2 (inter or intragranular), amount of oxide stabilizers, and difference in coefficient of thermal expansion, among others (Kelly and Rose, 2002; Quinn *et al.*, 2003).

2.5 Classification of zirconium based ceramics

Although many types of zirconia-based ceramics are available, three zirconia-containing systems have been used in dentistry (Kosmač *et al.*, 1999). Two of them are bi-phasic materials: glass-infiltrated zirconia-toughened alumina (ZTA) and the magnesium partially-stabilized zirconia (Mg-PSZ); the third type is the Yttria partially-stabilized tetragonal zirconia polycrystalline (3Y-TZP), a mono-phasic material which is used commonly.

In-Ceram zirconia is a glass-infiltrated zirconia-toughened alumina (ZTA), in which, for the first time, zirconium oxide was used as a dental ceramic. Due to its meta, stable nature, zirconia is a high-performance ceramic material (Bocanegra-Bernal and De La Torre, 2002). High-strength cores are composed of 67 wt. % of aluminium oxide and 33% of 12 mol% cerium-partially stabilized zirconium oxide; therefore, zirconia crystals (grain size <1 µm) are embedded in an alumina matrix (larger grains <2–6 µm, high elastic modulus). In such a composition that yields the highest tenacity and flexure strength inside this class of ceramics (400–800 MPa): micro cracks may trigger the so-called "transformation toughening" of zirconium, however a crack tip is more often seen to propagate through the alumina matrix surrounding the transformed crystals (Olsson *et al.*, 2003; Raigrodski, 2005). ZTA can be manufactured according to two different processes: soft machining or slip casting.

The latter presents the advantage of a more limited shrinkage but, at the same time, higher porosity and poorer mechanical properties than yttrium partially-stabilized tetragonal zirconia polycrystalline (3Y-TZP) (Guazzato *et al.*, 2004). 3Y-TZP is the strongest and most commonly used zirconia-based ceramic. Moreover, stabilization by cerium oxide provides better thermal stability and resistance to low temperature degradation (LTD) than Y-TZP (Sundh and Sjögren, 2004; Fischer *et al.*, 2009).

Magnesium, partially-stabilized zirconia microstructure (Mg-PSZ) consists of clusters of tetragonal crystals within a cubic stabilized zirconia matrix. The added stabilizer is MgO (8–10% mol) (Kelly and Denry, 2008). With regards to dental applications, with some exceptions (Denzir-M–Dentronic AB), such a material has not been extensively used, neither has it encountered large popularity due to its remarkable porosity, large grain size (30–60 μm), low stability, tendency to framework wear, and overall poor mechanical properties, especially when compared to 3Y-TZP (Hannink *et al.,* 2000).

The third common zirconia is yttrium partially-stabilized tetragonal zirconia polycrystalline (3Y-TZP). This type of zirconia is made of transformable, t-shaped grains stabilized by the addition of 3 mol% yttrium-oxides (Y_2O_3) (Abduo *et al.,* 2010). It is placed in category 4-polycrystalline solids (alumina and zirconia) and has no glassy components. All the atoms are packed into a regular pattern making it dense and stronger.

2.6 Properties of zirconia

Physical properties of zirconia such as hardness and chemical stability have been reported as early as 1945 (Geller and Yavorsky, 1945). The Young's modulus of zirconia is comparable to stainless steel alloys with superior strength, toughness and it is chemically and dimensionally stable (Piconi and Maccauro, 1999). This highly crystalline structure and composition contribute to its improved mechanical properties of zirconia ceramics as compared to feldspathic ceramics (Tinschert *et al.,* 2000; Guazzato *et al.*, 2004; Guazzato *et al.*, 2005). Unlike other ceramics, which fracture due to applied loads as a result of the development of cracks, in zirconia ceramics, the cracks formed under load are constricted and stopped and do not progress further (Špehar and Jakovac, 2015). Credit for the excellent strength of zirconia goes to the property known as transformation toughening.

2.7 Transformation toughening of zirconia

Phase transformation can occur in zirconia under certain forms of stress which are known as transformation toughening (Garvie *et al.*, 1975). The transformation of zirconia from the *t*→*m* phase can occur as a consequence of high temperature (thermal aging), grinding, or/and sandblasting (Garvie *et al.*, 1975; Chevalier *et al.*, 1999; Kosmač *et al.*, 1999). This transformation accompanies a volumetric change of 3–4%, which consequentially develops compressive stresses locally in the zirconia mass preventing crack propagation from the crack tips. This phenomenon has been described as transformation toughening (Pittayachawan *et al.*, 2009). The three classes of transformation toughened zirconia along with some examples have been tabulated in Table 2.2.

Table 2. 2 The three classes of transformation toughened zirconia along with some examples (Garvie *et al.*, 1975; Kelly and Denry, 2008)

Stabilized zirconia	**Types**	**Dental Examples**
Zirconia (dispersed phase) toughened ceramics	ZTA (alumina) ZTM (mullite)	In-Ceram zirconia (Vita Zahnfabrik)
Partially stabilized zirconia (PSZ)	Ca-PSZ Mg-PSZ Y-PSZ	Denzir-M (Dentronic AB)
Tetragonal zirconia polycrystals (TZP)	Y-TZP Ce-TZP	DC Zirkon (DCS Precident, Schreuder & Co) Cercon (Dentsply Prosthetics) Lava (3M ESPE) In-Ceram YZ (Vita Zahnfabrik)

2.8 Stabilization of zirconia

Conventional zirconia is not suitable for dental applications due to its volumetric shrinkage consequent to the phase transformation (*t*→*m*) upon cooling. Hence, it is stabilized using various oxides like MgO, CaO, Y_2O_3, CeO_2, etc. to render them useful for dental applications (Kelly and Denry, 2008).

The earliest investigations on zirconia were focused on the effects of oxide additions to reduce porosity and to increase its mechanical strength. By examinations with a heated X-ray camera, in studies as early as 1916, it has been demonstrated that the monoclinic-tetragonal inversion of pure zirconia takes place somewhere between 800°C and 1200°C, and that addition of certain oxides resulted in the formation of the stable cubic form (Geller and Yavorsky, 1945; Raffaelli *et al.*, 2008). Upon cooling, at room temperature, the phases became unstable crumbling up into multi-grained powders. The phase stabilization with aliovalent ion oxides facilitates the retention of tetragonal structure hence controlling the stresses induced at room temperature (Evans and Cannon, 1986).

Addition of these oxides to pure zirconia stabilizes the cubic phase resulting in partially stabilized zirconia (PSZ). PSZ is a multiphase material with c, m and t phases in the similar order of importance (Hisbergues *et al.*, 2009). A study showed that alloying with oxides of lower valance reduced the strained m phase at room temperature favoring more symmetric c and t phases (Garvie and Nicholson, 1972).

To date, three zirconia based ceramic systems have been used in dentistry. These are “yttrium cation-doped tetragonal zirconia polycrystals”, “magnesium cation-doped partially stabilized zirconia” and “zirconia-toughened alumina” (Denry and Kelly, 2008). However, other oxide stabilized zirconia ceramics are being studied extensively and shown to possess excellent properties.

2.9 Methods of stabilization of zirconia with oxides

Several researchers have used different methods to stabilize zirconia. In one of the earliest reported study on the stabilization of zirconia using oxides, the method involved a simple mixing of the zirconia and oxide in the required proportion and pressing at 10,000 lb/in^2 followed by firing in an oxyacetylene furnace at 2000 °C for 2 hours (Duwez *et al.*, 1952). In their study on stabilization of zirconia using calcia and magnesia, the authors reported that the minimum amount required for either oxide is 16 mol%. It was shown that both oxides were in solid state in cubic zirconia, which extended from 16 to 30 mol% for calcium, and from 16 mol% to 25 mol% for magnesia. It was also shown that the calcia stabilized zirconia remained cubic but the magnesia stabilized zirconia reverted to the monoclinic form upon heating at different ranges of temperature (Duwez *et al.*, 1952).

Researchers have also stabilized zirconia during the process of the synthesis of zirconia itself. In a study, researchers used the wet chemical method to synthesize Y-TZP powder from nitrate salts which were yttrium nitrate and zirconyl nitrate (Pandey and Biswas, 2014).

2.10 Different types of zirconia ceramic materials available for dental applications

2.10.1 Yttrium tetragonal zirconia polycrystals (3Y-TZP)

Since the last three decades 3mol% yttria ($Y2O_3$) has been used as a stabilizer to prepare biomedical grade zirconia (3Y-TZP) (Burger *et al.*, 1997). 3Y-TZP is primarily utilized to fabricate hip replacement prostheses due to its superior flexural strength ranging from 900-1200 MPa and good fracture strength ranging from 9-10 MPa $m^{1/2}$ (Christel *et al.*, 1989; Van der Zel, 2007). Its use has been reduced up to 90% due to a number of clinical failures reported (Piconi and Maccauro, 1999). 3Y-TZP has been used for fixed partial dentures and crown fabrication in dentistry. The prosthetic fabrication requires soft or hard machining to achieve desirable size and shape. The grain size of the zirconia particles greatly influences the mechanical properties of 3Y-TZP (Berger *et al.*, 2009).

Grain size larger than a certain limit makes 3Y-TZP less stable and additionally vulnerable to spontaneous phase transformation. Grain sizes <1 mm have been related to a lower transformation rate. However, grain size less than 0.2 mm makes it impossible to attain phase transformation which resulting in reduced fracture toughness (Ruiz and Readey, 1996). Consequently, the sintering conditions (through which the grain size is controlled) have a powerful impact on the stability and mechanical properties of the final product. Higher sintering temperatures and longer sintering times leads to a larger grain size (Chevalier *et al.*, 2004). Currently available 3Y-TZP utilizes sintering temperatures ranging between 1350°C and 1550°C depending upon the manufacturers recommendations for dental purposes. Soft machining method allows sintering at a later stage which prevents the stress-induced transformation from tetragonal to monoclinic. This allows the final surface nearly free of monoclinic phase unless grinding or sandblasting is performed. 3Y-TZP blanks manufacturers do not recommend grinding or sandblasting for dental applications to avoid both the phase transformation and surface crack propagation that could affect the long-term performance. In contrast, hard machining exhibits a larger phase of monoclinic zirconium oxide. This is often sometimes related to surface small cracks, lower reliability and higher susceptibility to low temperature degradation (LTD) (Guazzato *et al.*, 2004).

Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) also known as yttria stabilized zirconia (Y_2O_3, diyttrium trioxide) has been widely used for its superior mechanical properties. Its high flexural strength (up to 900–1200 MPa) (Santos *et al.*, 2016) and comparatively the highest fracture toughness (5.9 to 10 MPa $m^{½}$) supports a tetragonal structure (Raffaelli *et al.*, 2008). The yttria addition to zirconia leads to the stabilization facilitating the t and c phase (Tsunekawa *et al.*, 2003). Y-TZP have