SYNTHESIS AND CHARACTERIZATION OF ZIRCONIA-CALCIA NANOCOMPOSITE FOR DENTAL APPLICATION

NUR ATIKAH BINTI AB GHANI

UNIVERSITI SAINS MALAYSIA

2022

SYNTHESIS AND CHARACTERIZATION OF ZIRCONIA-CALCIA NANOCOMPOSITE FOR DENTAL APPLICATION

by

NUR ATIKAH BINTI AB GHANI

Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science

June 2022

ACKNOWLEDGEMENT

First, I would like to take this opportunity to thank my main supervisor, Assoc. Prof. Dr. Zuryati Ab Ghani for valuable guidance and constant encouragement throughout this project. Her continuous motivation, prolific ideas, constructive criticism and maintenance of friendly work environment has helped me a lot.

I want to convey my greatest gratitude towards co-supervisors, Dr. Tang Liszen, Dr. Yanny Marliana Binti Baba Ismail and Associate Professor Dr. Zaihan Bin Ariffin for their generous support, coaching and supervision during my study. Also, I am grateful to Prof. Dr. Ismail Ab. Rahman for guiding and teaching me fruitful lessons from his knowledge.

Besides, I want to thank to all the technical staffs especially Mr. Mohd Yusof Soon Abdullah, Mrs. Nora Aziz, Mr. Abdul Rahman Mustaffa and Mr. Muhamad Zulhilmi Mohd Nor for their invaluable help. I would like to thanks to postgraduates' colleagues and friends especially Ahmad Nazeer Che Mat, Abdul Manaf Abdullah, Mohd Nazrulhuzaimi Md Yusoff, and Wan Nur Fadilla Wan Hamad who had helped me throughout my research and sharing so much ideas and opinions about the project. I would like to express my appreciation to USM short term research grant (304/PPSG/6315034) for the financial assistance.

Last but the most affectionate acknowledgment is to my parents for their support either mentally and financially. My special and deepest thanks to my husband for support, believing, encouragement and endless love throughout the project and standing beside me. By and large, this thesis was the output of the hard work and cooperation from all parties besides my own effort.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF SYMBOLS

°	Degree
%	Percentage
%T	Percentage of Transmittance
°C	Temperature
θ	Theta
°	Degree

LIST OF ABBREVIATIONS

BET	Brunauer- Emmett-Teller
EDX	Electron Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscope
FTIR	The Fourier Transform Infrared
g	Gram
ISO	International organization for standardization
M	Molar
ml	Millimeter
mm	Millimeter
MPa	Mega pascal
nm	Nanometer
rpm	Revolutions per minute
s	Second
SBF	Simulated body fluid
SD	Standard deviation
TEM	Transmission Electron Microscope
TGA	Thermogravimetric analysis
VHN	Vickers microhardness
XRD	X-ray diffraction

LIST OF APPENDICES

Appendix A	Instruments used in the study
Appendix B	Calculation of preparation study
Appendix C	Statistical analysis
Appendix D	Ethical approval

SINTESIS DAN PENCIRIAN ZIRKONIA-CALCIA NANO KOMPOSIT UNTUK APLIKASI PERGIGIAN

ABSTRAK

Kajian ini telah direka bentuk untuk mengkaji zirconia yang distabilkan oleh nano kalsium oksida (CSZ) yang disintesis dengan kaedah sol-gel sebagai potensi bahan implan pergigian, substruktur untuk mahkota dan jambatan pergigian. Beberapa parameter seperti tindakbalas media, kepekatan bahan tambah organik dan kepekatan agen pemendakan dikaji. Serbuk calcia-zirconia yang optimum dipilih dan dimampat dalam acuan keluli tahan karat menggunakan penekan hidrolik di bawah tekanan 5 tan (60 MPa). Sampel yang dimampat disinter pada suhu berbeza iaitu 1200, 1300 and 1400 °C selama dua jam. Kajian bioaktiviti bagi sampel yang disinter pada suhu 1400 °C dikaji keupayaan untuk membentuk apatit di permukaan di dalam larutan simulasi badan (SBF) untuk jangka masa yang berlainan dalam 4 minggu pada suhu 37.0 °C. Dengan kehadiran 2.0 M NH_3 dalam larutan etanol, serbuk calcia-zirconia berjaya diperoleh di mana partikel-partikel tersebut mempunyai bentuk sfera dengan penggumpalan yang kurang dan mengandungi ukuran skala nano antara 40 hingga 80 nm dengan keluasan permukaan BET tertinggi iaitu 43.65 m^2/g. Pelet CSZ1400 menunjukkan fasa kubik zirkonia dalam analisis XRD, manakala tekstur halus selepas digilap diperoleh dalam analisis FESEM. Pengukuran ketumpatan menunjukkan bahawa CSZ1400 mempunyai ketumpatan relatif optima iaitu 94.95±1.013 %. Nilai mikrokekerasan Vickers bagi CSZ meningkat dengan peningkatan suhu pensinteran dari 435.17±27.89 hingga 640.11±31.97 HV (4267±273.58 hingga 6277±313.44 MPa), di mana CSZ1400 sebanding dengan CEREC zirconia ($p > 0.05$). Kajian bioaktiviti bagi CSZ1400 menunjukkan pembentukan lapisan apatit di permukaan, dimana menunjukkan keserasian bio dan keupayaan membentuk tulang. Kajian fizikal, mekanikal dan biologi membuktikan bahawa zirconia yang distabilkan CaO menggunakan proses ‘sol-gel' dapat digunakan sebagai alternatif kepada zirconia semasa yang terdapat di pasaran untuk aplikasi pergigian.

SYNTHESIS AND CHARACTERIZATION OF ZIRCONIA-CALCIA NANOCOMPOSITE FOR DENTAL APPLICATION

ABSTRACT

This study was designed to examine zirconia stabilized by nano calcium oxide (CSZ) synthesized using sol-gel method as for potential material for dental implant, dental crown and bridgework substructures. Some parameters such as medium of reaction, concentrations of organic additive, and concentration of precipitating agents were investigated. The optimum calcia-zirconia powder was selected and pressed in stainless steel mould using a hydraulic press under 5 tons (60 MPa) pressure. The pressed samples were sintered at different temperatures of 1200, 1300 and 1400 °C for 2 hours. The bioactivity study was carried out on the pressed samples sintered at 1400 °C to examine the ability of apatite formation on its surface in a simulated body fluid (SBF) solution for different periods within 4 weeks at 37.0 °C. In the presence of 2.0 M NH_3 in ethanolic solution, calcia-zirconia powder was successfully obtained, where the particles were spherical in shape with less agglomeration, and consisting of a nanoscale dimension ranging from 40 to 80 nm with the highest BET surface area of 43.65 m^2/g. The CSZ1400 pellet showed cubic phase zirconia with XRD analysis, and it gave the smoothest texture after polishing when viewed under FESEM images. Density measurement of CSZ1400 produced an optimum relative density value of 94.95±1.013 %. The values of Vickers microhardness of CSZ were increased with the increase in sintering temperatures ranging from 435.17±27.89 to 640.11±31.97 HV (4267±273.58 to 6277±313.44 MPa), where CSZ1400 was comparable with CEREC zirconia ($p>0.05$). The bioactivity test on CSZ1400 revealed the apatite layer formation on its surface which indicated the biocompatibility and potential bone forming ability. Physical, mechanical and biological study proved that CaO stabilized zirconia using sol-gel method may be used as an alternative to the current zirconia available in the market for dental application.

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

As age increases, the problem of tooth loss becomes a major issue that needs to be addressed. In dentistry, restorative materials such as crowns, bridges and implants are some of the common ways to overcome the lost tooth structure. Basically, the restorative material used is contingent with the degree of destruction of the tooth where their functions and appearances must be similar to that of the natural tooth. Fixed dental prostheses (FDPs) which refer to crowns and bridges have previously been done with metals or metal substructures veneered with porcelain for aesthetic purposes. Several laboratory steps are involved in this type of crown and bridges construction. Currently, with chair side computer-aided design/ computer-aided manufacturing (CAD/CAM) technology, the construction of FDP, especially crown can be prepared chairside, during a single visit using ceramic ingot.

In the fabrication of fixed dental prostheses (FPD), zirconia-based ceramics have been used to replace non aesthetic dental alloy as framework underneath the brittle veneering porcelain (Abduo *et al*, 2010). Lately, zirconia-based ceramics have been used as their aesthetic properties improve to construct the whole crown and bridge rather than just as framework due to the concern regarding allergy and toxicity effect of certain alloys (Madfa *et al*, 2014). Also, zirconia dental implants present interesting property through *in vitro* and *in vivo* studies where it has a low affinity to bacterial plaque, small amounts of inflammatory infiltrate and excellent soft-tissue integration (Cionca *et al*, 2017). These characteristics may help to reduce the risk of peri-implant disorders. However, due to its peculiar arrangements of atoms, zirconia (ZrO_2) turns out to be very hard (Hambire & Tripathi, 2013) which may cause wear to the milling machine during construction of dental crown and bridgework. The addition of stabilizing oxides such as yytria (Y_2O_3), magnesia (MgO), ceria (CeO_2) and calcia (CaO) to the pure zirconia will obtain a multiphase material, which makes it completely or partially stabilized zirconia, thus enable them to be used for dental application (Zivko-Babic *et al,* 2005). The definition of multiphase material is that there is more than one unique component in it, and the compounds create different regions in the substance with varied characteristics.

Three zirconia-containing ceramic systems have been developed and used to date in dentistry namely yttrium cation-doped tetragonal zirconium polycrystals (3Y-TZP), zirconium-toughened alumina (ZTA), magnesium cation-doped partially stabilized zirconium (Mg-PSZ), and ceria-stabilized zirconia-alumia (CeTZP/A) (Denry & Kelly, 2008; Tanaka *et al,* 2002). However, some issues such as low temperature aging degradation, lower reliability, low mechanical properties, large grain size and high porosity retard its performance for dental purposes. For example, Y-TZP possesses a high fracture toughness of 5-10 MPa $m^{1/2}$, and a flexural strength of 900–1400 MPa (Miyazaki *et al*, 2013; Osman & Swain, 2015) which can be milled either fully sintered blocks or partially sintered blocks (green blocks) using CAD/CAM procedures suffered from low-temperature aging degradation (LTAD) caused by phase transformation (Hannink *et al*, 2000). Ce-TZP/A is the toughest dental ceramic material currently available, with a fracture toughness of approximately 19 MPa $m^{1/2}$ and a flexural strength of approximately 1400 MPa (Tanaka *et al,* 2002) may cause wear to the milling machine. Mg-PSZ contained 8 – 10 mol % of Mg seems to be not suitable for dental application due to the presence of high porosity, large grain size (30 – 60 μm) that cause wear to the opposing structure, low stability and low mechanical properties (El-Ghany & Sherief, 2016).

Instead of the above aforementioned stabilizers, calcia (CaO) also has been widely used to stabilize ZrO_2 for various applications such as solid electrolyte for battery (Muccillo *et al*, 2001), sensor (Zhou & Ahmad, 2006), solid oxide fuel cell (Merino *et al*, 2004) and in biomedical applications (Fassina *et al*, 1992). In medical applications, the usage of CaO is important due to its biocompatibility. Research on hip replacement implant utilizing calcia stabilized zirconia (CSZ) by Nath *et al.*, (2008) exhibited Vickers hardness of 8–10 GPa, a modest fracture toughness (6 MPa $m^{1/2}$) (Nath *et al*, 2008). These properties are better than commercial grade alumina, however lower than Y-TZP and CeTZP/A. The moderate mechanical properties of CSZ in those studies indicated that CSZ is a suitable material for dental application, where it can provide optimum strength while preventing wear to the CAD/CAM milling machine.

Furthermore, the morphological shape and particle size of $CaO\text{-}ZrO_2$ are scarcely reported in the literatures especially for dental purposes. One of the studies produced CaO nanoparticles derived from cockle shells, which was physically mixed with zirconia to produce calcia stabilized zirconia (Hussein *et al*, 2020). The technique used in that study maybe less effective because the movement of particles was two dimensional, and the materials may not be fused together during sintering. Hence, this current study was focussed on synthesizing spherical and nanosized CSZ using sol-gel method and tested for dental application. Incorporation of CaO by sol-gel technique can produce better microstructure of CaO stabilised zirconia and improve the material properties.

1.2 Problem Statement

The use of CaO to stabilize zirconia for dental application are scarcely reported in the literatures, even though sintered calcia partially stabilized zirconia for hip replacement implant has been reported to exhibit Vickers hardness of 8-10 GPa and fracture toughness of 6 MPa $m^{1/2}$ (Nath *et al*, 2008). Another study produced CaO nanoparticles derived from cockle shells, which was then physically mixed with zirconia to produce calcia stabilized zirconia and it exhibited a moderate Vickers hardness of 977 MPa (Hussein *et al*, 2020). This is lower in comparison to the Vickers hardness of Ce-TZP was around 1200 MPa (Benzaid *et al*, 2008; Hu & Wang, 2010), and 10Ce-TZP with hardness value of 6200 MPa (Turon-Vinas *et al*, 2018). The hardness achieved by Hussein *et al*., in 2020 has made their material friendly to the milling machine, and possibly less abrasive to the opposing teeth. However, the technique used in that study was less effective because the movement of particles was limited due to physical mixing. Furthermore Hussein *et al*., (2020) did not report on the bioactivity of the fabricated calcia stabilized zirconia derived from cockle shell. The bioactivity is an important indicator with regards to the suitability of that particular material as a potential dental implant, which allows it to form a bond with living tissue (Alagiriswamy et al, 2020). Regardless of the addition of stabilizing, zirconia is a bio-inert material, which may have an impact on osseointegration capability. Hence, studies focusing on surface treatments of zirconia to render the surface more receptive to osseointegration and apatite formation have gained prominence. Also, *in vitro* testing such as simulated body fluid (SBF) analysis have been used to mimic *in vivo* conditions, thereby decreasing time, cost, and regulatory concerns, and it can be altered in controlled manner by researchers (Alagiriswamy et al, 2020). Therefore, synthesizing spherical and nanosized calcia stabilized zirconia (CSZ) using sol-gel method is thought to produce a better material with good microstructure, suitable hardness and with promised bioactivity for dental application.

1.3 Justification of the study

If CSZ can be successfully fabricated using sol-gel method, it could be a potential zirconia material to have better hardness, density, and other properties than other commercially available zirconia that can give optimum strength but at the same time does not wear the CAD/CAM milling machine. If its hardness is lower than the current zirconia available in the market, then this new zirconia material may cause less abrasion to the opposing teeth. Therefore, this material has a potential to be an alternative zirconia material with properties more suited for use in dentistry, especially in dental crown and bridgework, as well as dental implant.

1.4 Scope of the Study

In this study, $CaO-ZrO_2$ was developed by sol-gel method and tested for dental applications. Some parameters such as medium of reaction, concentrations of surfactant, and concentration of precipitating agents were investigated in order to understand their effects on the morphology, physical and mechanical properties of CSZ such as the surface structure, crystallinity, chemical bonding, porosity, density and hardness. After the synthesis of $CaO-ZrO_2$, the powder was tested for its thermal stability using thermogravimetric analysis (TGA). The sample was heated from room temperature to 900°C at a heating rate of 5°C/min in air. The prepared $CaO-ZrO_2$ powder was characterized using XRD to determine the crystallinity and phases. The surface morphology of the specimens was investigated using FESEM and TEM, while the elemental compositions of $CaO-ZrO_2$ was determined using EDX. The FTIR spectrometer was used to determine the chemical bonding of the prepared powder. The specific surface area and pore size distribution of a composite was measured by BET (Brunauer- Emmett-Teller) method. The CSZ pellets were sintered at different temperatures ranging from 1200 - 1400 °C. The crystallinity and morphology of the sintered pellets was investigated again with XRD and FESEM analyses. The Vickers microhardness and density tests were then performed to evaluate the physical and mechanical properties. The bioactivity of the sintered pellets was also evaluated by examining the ability of apatite formation on the surface in a simulated body fluid (SBF).

1.5 Objectives

1.5.1 General objectives

The objective of this study was to synthesize and characterize calcia stabilized zirconia (CSZ) for dental application.

1.5.2 Specific Objectives

1. To synthesize a range of CaO-ZrO_2 nanoparticle powders using sol-gel method and characterize them.
2. To investigate the effect of sintering temperatures on the physical and mechanical properties of CSZ pellets and compare them with CEREC Zirconia.
3. To study the bioactivity of the sintered CSZ pellet *in-vitro.*

1.6 Research Question

1. Could CaO-ZrO_2 powder be synthesized by sol-gel method?
2. What is the effect of sintering temperatures on physical and mechanical properties of CSZ pellets?
3. Are the sintered CSZ pellets bioactive in *in-vitro* study?

1.7 Research hypothesis

1. Sol-gel method could be used to synthesize $CaO\text{-}ZrO_2$.
2. Higher sintering temperature could improve the physical and mechanical properties of CSZ pellets.
3. The *in vitro* bioactivity of the sintered CSZ pellets through simulated body fluid could produce apatite on the surface of the material.

CHAPTER 2

LITERATURE REVIEW

2.1 Dental restorative materials

Dental restoration is a treatment used to restore the function of missing tooth structure resulting from caries or external trauma. Material selection, which includes surface texture, shape, translucency and shading are required to produce natural looking dental restoration (Shahmiri *et al*, 2018). Tooth restoration can be made from a variety of different materials which have their unique advantages and are suited for different uses and situations. Restorative dental materials are required to meet the performance standards established by the Food and Drug Administration (FDA) or other standards such as American Dental Association (ADA) and International Organization for Standardization (ISO). To meet decent requirements, the material is proposed to be mechanically stable and durable, biocompatible and esthetic (Anusavice *et al*, 2012; Porto *et al*, 2019). The mechanical properties of the materials should be strong and resistant to fracture. Besides, the materials should be non-toxic, non-irritating, and non-allergenic. The esthetic should also look like natural tooth structure.

One of the important materials that are mainly used as implants in medical and orthopedic field is bio ceramics. This material is usually used for regeneration of defected human bone, teeth, joints and skeleton (Thamaraiselvi & Rajeswari, 2004). As illustrated in Figure 2.1, ceramics such as alumina, zirconia and lithium disilicate are employed nowadays depending on clinical use. As stated by Bona *et al*., (2015), silica-, leucite-, lithium disilicate-, alumina-, and zirconia-based materials are most popular used in dental ceramic systems. The popularity of all-ceramic materials has increased because of their chemical stability, excellent aesthetics, and biocompatibility (Powers *et al*, 2012; Van Noort & Barbour, 2014).

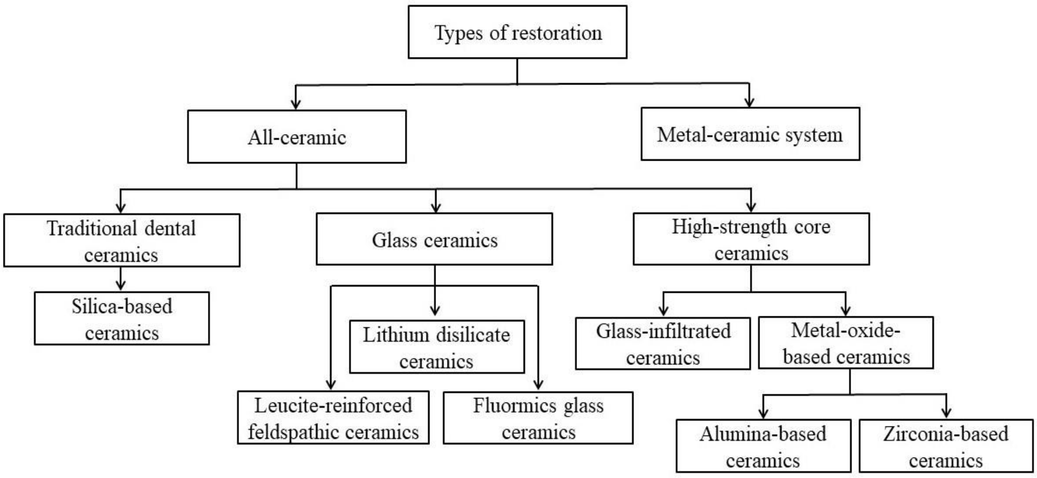

Figure 2.1 Classification diagram by the type of restoration (Fornabaio *et al*, 2017)

2.2 Dental ceramics materials

Dental ceramics is defined as an inorganic compound which is made essentially from a non-metallic organic material containing oxygen and one or more metallic or semimetallic elements. This material is usually processed by firing at high temperature to achieve desirable properties (Powers *et al*, 2012). Dental ceramic is a popular choice for restoration such as crowns, veneers and bridges because it is strong and durable, and also it is aesthetics. Pittayachawan (2009) stated that ceramics can be classified into four categories, which are silicates, oxides, non-oxides and glass. Silicate ceramics are characterized by an amorphous glass phase and their porous structure, of which the main component of silicate ceramic is SiO_2 with addition of small crystalline Al_2O_3, MgO, ZrO_2 and/or other oxides. Example of silicate ceramic used in dental industry is dental porcelain (Anusavice *et al*, 2012). Oxide ceramics contain a crystalline phase such as (Al_2O_3, MgO, ZrO_2), with either no glass phase or a small amount of glass phase (Anusavice *et al*, 2012).

In dentistry, non-oxide ceramics are impractical because of high processing temperature, opacity, complex processing procedure and unaesthetic color (Anusavice *et al*, 2012). Glass ceramics are partially crystallized glasses, which occur by nucleation and growth of crystal in the glass matrix. Dicor glass ceramic is one of the examples of glass ceramic (Anusavice *et al*, 2012).

Ceramic has replaced traditional materials, for example silver amalgam due to the demand for environmentally friendly materials. The existing non-zirconia dental ceramics, which include feldspathic porcelain and glass ceramics generally provide good esthetic results when bonded to non-discolored tooth structure because of their light transmission (Shahmiri *et al*, 2018). This material is color stable as can be easily colored to match the natural color of any tooth. However, dental ceramic is more brittle compared to other materials, which the tooth cannot withstand the pressure of chewing and biting, especially for molar teeth (Powers *et al*, 2012).

Then, dental zirconia was introduced in dentistry because it is highly durable. It is a non-metallic substance derived from metal. The metal–zirconia is chemically altered in a process that gives its durable crystalline structure. The durability and usefulness of zirconia is similar to composite resin. Basically, the demand for the use of zirconia is often about its aesthetics compared to composite resin that is more translucent. Generally, zirconia restoration lasts longer than porcelain. Porcelain crowns need to be replaced after a few years, nevertheless zirconia crowns have shown a 99% survival rate after five years (Raigrodski *et al*, 2012). Zirconia-based ceramics have been used to replace non aesthetic dental alloy as framework underneath the brittle veneering porcelain in the fabrication of fixed dental prostheses (FPD) (Abduo *et al*, 2010). Zirconia-based ceramics are the most studied ceramics (Bona *et al*, 2015). Due to its peculiar arrangements of atoms, zirconia (ZrO_2) can be a very hard material (Hambire & Tripathi, 2013). The addition of stabilizing oxides such as yttria (Y_2O_3), magnesia (MgO), ceria (CeO_2) and calcia (CaO) to the pure zirconia will obtain a multiphase material, which makes it completely or partially stabilized zirconia, thus enable it to be used for dental application (Zivko-Babic *et al*, 2005).

2.3 Dental Ceramics used with CAD/CAM system

The development of advanced dental ceramics has led to the application of partially stabilized zirconia in restorative dentistry, which can be produced from a computer-assisted design/computer-aided manufacture (CAD/CAM) system. The details of the restoration tooth are designed with the aid of a computer and milled by a milling machine as shown in Figure 2.2 (Miyazaki *et al*, 2009). The advantages of the CAD/CAM system are it can produce a restoration in one visit, which minimizes human mistake or laboratory fabrication process and reduce the time taken to produce the restoration, since the traditional method usually include impression taking, creating a model or die making and manufacturing the final product (Pittayachawan, 2009).

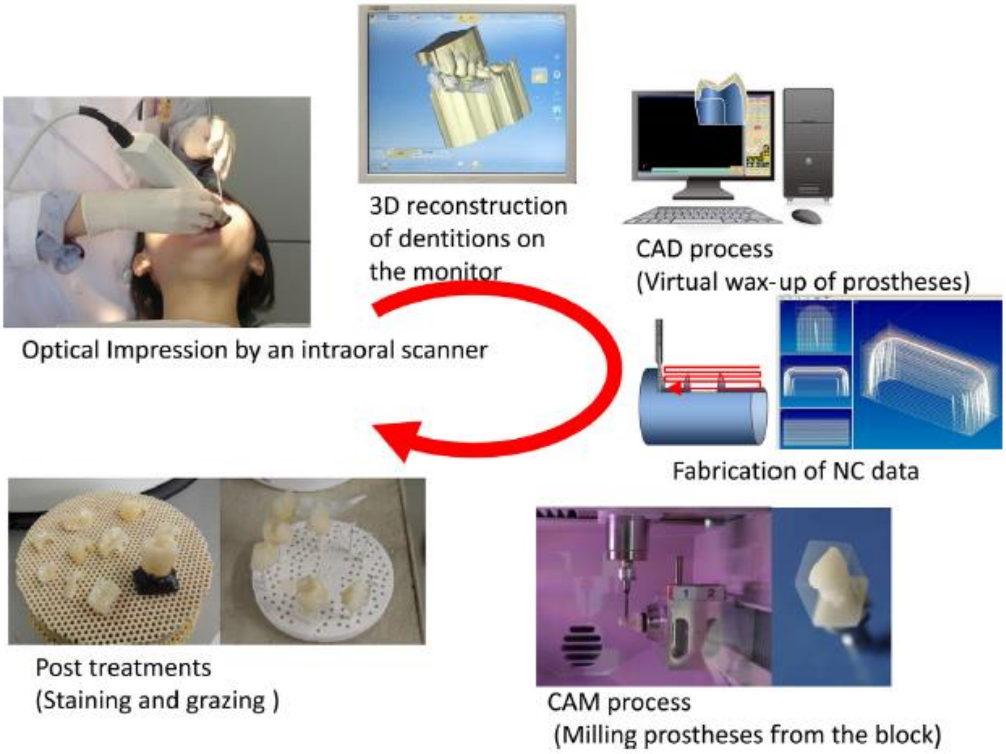

Figure 2.2 Process of digital fabrication system (Miyazaki *et al*, 2009)

Several ceramic materials as shown in Table 2.1 are available in the market for use as a CAD/CAM restoration (Pittayachawan, 2009). Machinable ceramic such as Dicor and Vita Mark II were used in earlier CAD/CAM restoration, which were successfully used as inlays, onlays, veneers and crowns. An ideal choice for higher aesthetics stated by Liu (2005) is In-Ceram Spinell, considered for anterior crowns with a strength of 350 MPa. In-Ceram alumina has high translucency and strength of 525 MPa, which can be considered for anterior/posterior crowns and three-unit anterior bridges. Nevertheless, all materials mentioned are not strong enough to sustain an occlusal load (Liu, 2005). Therefore, alumina and zirconia were chosen for posterior restoration due to their strengths of 750 MPa and 1000 MPa, respectively (Liu, 2005). In high-stress areas, especially for posterior crowns and multiple-unit posterior, In-Ceram zirconia or Yttrium-reinforced zirconia may be used (Pittayachawan, 2009). Fully sintered alumina or zirconia were difficult to mill, and basically milling occurs at pre-sintered stage (Liu, 2005; Pittayachawan, 2009).

Table 2.1 Restorative materials used for CAD/CAM systems (Pittayachawan, 2009)

Restorative material	Indications	Flexural strength (MPa)
Dicor MGC (fluoromica)	Inlays, onlays, veneers	<100
Vita Mark II (feldspathic)	Inlays, onlays, veneers, anterior crowns	150
ProCAD (Leucite reinforced)	Inlays, onlays, veneers, anterior crowns	150
In-Ceram Spinell (Magnesium oxide)	Anterior crowns	350
In-Ceram Alumina (Aluminum oxide)	Crowns and anterior bridges	500
Alumina (aluminium oxide)	Crown and bridge	600
In-Ceram zirconia (Zirconium oxide)	Crown and bridge	750
Partially sintered zirconia (Zirconium oxide)	Crown and bridge	800-1300
Fully sintered zirconia (Zirconium oxide)	Crown and bridge	>1000

2.4 Structural ceramics based in zirconia

Compared to other dental ceramic systems, the use of zirconia-based ceramics for dental restoration is increasing due to its biological, excellent mechanical and optical properties (Denry & Kelly, 2008; Guazzato *et al*, 2005). This has also accelerated its routine use in CAD/CAM system (Volpato *et al*, 2011). In engineering, zirconia-based ceramics are regularly used, especially in structural application, for example in the manufacture of cutting tools, gas sensors, refractories and also structural opacifiers (Rashad & Baioumy, 2008). Usually, zirconia is doped with stabilizers to meet structural demands. The currently used bioceramics in medical and dental care are derived from structural materials, which are used in aerospace and military armor. These materials were modified to suit the requirements of biocompatibility (Volpato *et al*, 2011).

2.4.1 Definition and history of zirconia

Zirconium is represented by the chemical symbol Zr, and its atomic number is 40. In the D.I. Mendeleev's periodic chart, zirconium is one of the transition metals as the atom has an incomplete d sub-shell. Zirconium exhibits in two forms, which are crystalline and amorphous form (Volpato *et al*, 2011). Zirconium has been known as zircon or zirconium silicate ($ZrSiO_4$) which composed of 67.2% of ZrO_2 and 32.8% of SiO_2 (Pittayachawan, 2009). Chemically extracted zirconate (ZrO_2-SiO_2, $ZrSiO_4$) or baddelyite (ZrO_2) may produce zirconium. Zirconium dioxide (ZrO_2), which is also known as zirconia that is produced from baddelyite is a course oxide that presents a monoclinic structure at room temperature. Nevertheless, zirconia powder may be purified and processed synthetically at high temperature to form a structure called cubic zirconia (Volpato *et al*, 2011). The modified material can give higher strength and toughness, optically flawless and translucent compared with other ceramics, which can be suited the requirement in different applications. This unique zirconia property is called transformation toughening.

2.4.2 Transformation toughening

Zirconia (zirconium dioxide, ZrO_2) is a polymorphic material, which can form in three different crystal structures, named tetragonal, monoclinic and cubic as shown in Figure 2.3. During heating or cooling, zirconia can be transformed from one crystalline phase to another (Pittayachawan, 2009). Only the monoclinic phase of ZrO_2 is stable from room temperature up to 1170 °C, after which it gets inverted into a metastable tetragonal phase. Zirconia turns into a cubic phase when temperature at above 2370 °C (Ghazinoory *et al*, 2009). In monoclinic form, the ZrO_2 has crystallographic phases of deform prism with parallelepiped sides. In tetragonal phase, a straight prism with rectangular sides has occurred. The high-temperature cubic phase exists square sides (Pittayachawan, 2009). Due to polymorphism, pure zirconia is unsuitable to be used at elevated temperature because of volume changes occurs during cooling. This change is adequate to exceed the elastic and fracture limits, which resulting in cracks and flaws (Denry & Kelly, 2008).

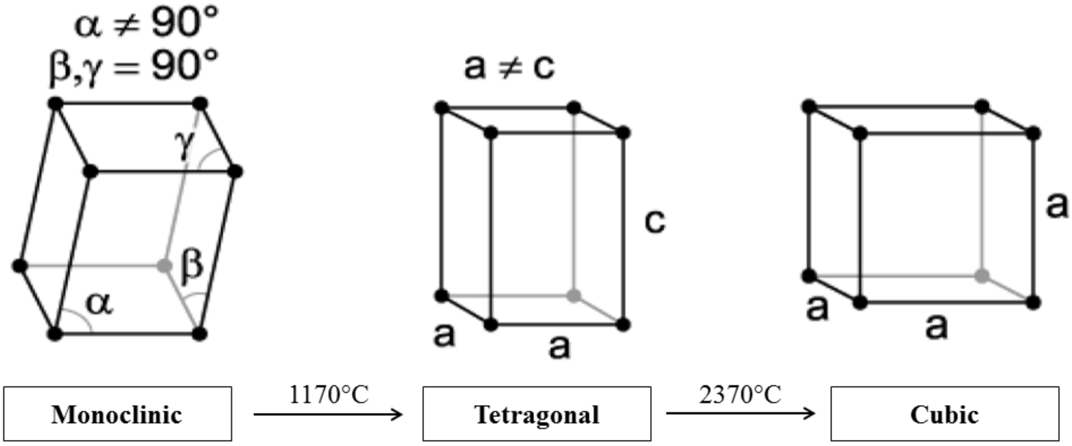

Figure 2.3 Crystallographic phases of zirconia (Pittayachawan, 2009).

The researchers have discovered that the phase relationships between zirconia and metal oxides, also known as stabilizer, such as CaO, MgO, Y_2O_3, or CeO may retain tetragonal or cubic phases at room temperature after sintering, thus it can control the stress-induced transformations. The phase transformation tends to induce volume expansion up to 3 – 4 % which lead to cracking (Leib *et al*, 2016). These phases also depend on the amount of oxides added, and basically were determined from the relevant phase diagram. (Duwez *et al*, 1952; Pittayachawan, 2009). The addition of stabilizer combined with changes in processes allows the formation of partially or fully stabilized zirconia, which result in exceptional properties such as high flexural strength and fracture toughness, high hardness, and good chemical resistance. Adding sufficient amounts of stabilizing oxides, such as 16 mol% magnesia (MgO), 16 mol% of limestone (CaO) or 8 mol% yttria (Y_2O_3) may obtain a fully stabilized zirconia. Partial stabilization of zirconia may be obtained with the same oxides, however in smaller amounts, which is a multiphase structure is created. This multiphase structure usually consists of cubic and tetragonal zirconia in majority, including small amount of monoclinic phase precipitated (Volpato *et al*, 2011).

2.5 Stabilization of zirconia

The earliest studies on zirconia were focused on the effects of oxide additions to improve its mechanical strength and reduce porosity. The examination with a heated X-ray camera in studies early 1916 demonstrated that the monoclinic-tetragonal inversion of pure zirconia takes place somewhere between 800°C and 1200°C, and with the addition of certain oxides resulted in the formation of the stable cubic form (Raffaelli *et al*, 2008). Upon cooling, at room temperature, the phases became unstable crumbling up into multi-grained powders. Addition of mentioned oxides to pure zirconia stabilizes the cubic phase, resulting in partially stabilize zirconia (PSZ). PSZ is a multiphase material with cubic, monoclinic and tetragonal 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 cubic and tetragonal phases. The addition of various amount of stabilizers allows the formation of different types of zirconia, for example Tetragonal Zirconia Polycrystals (TZP), Partially Stabilized Zirconia (PSZ), Fully Stabilized Zirconia (FSZ), Transformation Toughened Ceramics (TTC), Zirconia Toughened Alumina (ZTA), and Transformation Toughened Zirconia (TTZ) (Leal-Ayala *et al*, 2019). Table 2.2 shows the physical and mechanical properties of various types of doped zirconia products.

Table 2.2 Physical and mechanical properties of various types of doped zirconia (Leal-Ayala *et al*, 2019).

Property	**Y-TZP**	**Ce-TZP**	**ZTA**	**Mg-PSZ**
Density (g/cm^3)	6.05	6.15	4.15	5.75
Hardness (HV_{30})	1350	900	1600	1020
Bending strength (MPa)	1000	350	500	800
Compressive strength (MPa)	2000	-	-	2000
Fracture toughness (MPa m$^{1/2}$)	9.5	15-20	4-5	8-15

Relevant phase diagram can be utilized to define the required amount of alloying oxide to produce respective stabilization. On a basic level, any composition that is sintered in the cubic phase and retains a completely cubic crystal structure on cooling is considered as fully stabilized (Gautam *et al*, 2016). The continued possession of the tetragonal phase at room temperature will likewise be doable, given that the tetragonal to monoclinic phase transformation is inhibited. This can be accomplished by a combination of fine powders, matrix constraints and addition of stabilizer (Gautam *et al*, 2016).

2.6 Types of zirconia used in dentistry

In prosthetic dentistry, zirconia has been used for the fabrication of crowns and fixed partial dentures. Recently, zirconia containing ceramic was introduced as restorative materials, not only because of excellent mechanical properties and resistance to temperature, but also due to their biocompatibility (Leal-Ayala *et al*, 2019). In spite of the fact that there are so many different types of zirconia, however only three types of zirconia are used to date in prosthetic dentistry. Commercial zirconia-based ceramic that was used are yttrium cation-doped tetragonal zirconium polycrystal (3Y-TZP), magnesium cation-doped partially stabilized zirconium (Mg-PSZ), zirconium-toughened alumina (ZTA), and ceria-stabilized zirconia-alumina (Ce-TZP/A) (Denry & Kelly, 2008; Volpato *et al*, 2011).

3Y-TZP consists of approximately 2 to 3 mol percent of yttria oxide (Y_2O_3) as a stabilizing agent in ZrO_2 to allow the sintering of fully tetragonal fine-grained zirconia, usually less than 0.5 mm which could contain up to 98% of metastable grains (Gautam *et al*, 2016; Volpato *et al*, 2011). 3Y-TZP is used primarily to fabricate hip replacement prostheses because of its high flexural strength and good fracture strength. Then, it has been used in dentistry for fixed partial dentures and crown. Y-TZP which exhibit high fracture toughness ranging from 5 to 10 MPa $m^{1/2}$, and a flexural strength of 900–1400 MPa (Miyazaki *et al*, 2013; Osman & Swain, 2015) can be fabricated by milling either fully sintered blocks or partially sintered blocks using CAD/CAM procedures. However, it suffers from low-temperature aging degradation (LTAD) caused by phase transformation (Hannink *et al*, 2000).

Zirconia-toughened alumina (ZTA) is a structure that is fabricated by combining zirconia with a matrix of alumina (Al_2O_3). This material was reported that had high resistance to crack propagation, which can improve the lifetime and reliability of ceramic joint prosthesis (Gautam *et al*, 2016). The addition of 33 mol% zirconia stabilized with 12 mol% ceria (12Ce-TZP) was combined to the precursor In-Ceram Alumina matrix to produce the current commercial toughened ceramic known as In-Ceram Zirconia (Vita Zahnfabrik, Germany) (Gautam *et al*, 2016). Soft machining or slip casting technique was used to fabricate In-Ceram Zirconia. This technique limits the amount of shrinkage after sintering, however the amount of porosities were increased from 8 to 11 % (Guazzato *et al*, 2005). Other than that, Ce-TZP/A was fabricated by Tanaka *et al*., (2002), which reported had toughest dental ceramic material available, with a fracture toughness of 19 MPa $m^{1/2}$, and a flexural strength of 1400 MPa (Tanaka *et al*, 2002). However, this can be a drawback when this zirconia block is milled fully sintered, as it can wear the milling machine.

Magnesia partially stabilized zirconia (Mg-PSZ) was reported as unsuitable material used in dentistry due to its larger grain size and large porosities, which may lead to surface wear and crack propagation. The sintering temperature of Mg-PSZ is about 1680 to 1800 °C, which contributed higher temperature compared to other composites. Additionally, Mg-PSZ was reported as poor stability, which may slightly lower the energy for tetragonal to monoclinic phase transformation. Fully sintered Mg-PSZ have been manufactured, and it requires rigid and strong machining systems (Volpato *et al*, 2011).

2.7 Calcia Stabilized Zirconia (CaSZ)

The stabilization of zirconia with CaO was demonstrated as early as 1947 (Curtis, 1947). Curtis and his colleagues showed that stabilization of zirconia with CaO greatly improved the thermal shock resistance. It was noted that similar to Y-TZP, Calcia doped zirconia (CaO-PSZ) exhibits c, t, and m phases, however, CaO is naturally abundant and use of CaO as an alternative to Y_2O_3 could be economically beneficial (Drazin & Castro, 2016). Drain and Castro (2016) showed that when CaO is used as the dopant, the m→t phase transformation was achieved at 4.7 mol% of CaO and from t→c phase 8 mol% of CaO was noted. However, for Y_2O_3 m→t crossover was noted at 3.5 mol% and t→c at 11.3 mol%. For commercial purposed 7.5 to 8.7 mol% of CaO is added to manufacture CaO based partially stabilized zirconia (Hannink *et al*, 2000). The applications of CaO stabilized zirconia in dentistry have not been studied widely.

In a recent study, CaO stabilised zirconia was compared with silica stabilised zirconia to assess the mechanical properties and pH of the fabricated samples. The interaction between alloy and the zirconia coating was also studied. This study was performed primarily to implement the use of CaO to stabilise zirconia (Yuan *et al*, 2015). In another study different molarities of alumina were added to raw CaO stabilised zirconia to study its thermal conductivity, phase transformation and mechanical properties (Kim *et al*, 2016). The influence of different forms (hot isostatic) pressing conditions of Ca-doped stabilized zirconia dental ceramics on density, compressive strength, phase transformation, and Young's modulus has also been previously evaluated (Gionea *et al*, 2016a).

2.8 CEREC Zirconia Medi S A1

CEREC Zirconia Medi S A1 (Dentsply Sirona Dental System GmbH, Germany) is zirconia block made of zirconium-oxide for milling blocks. The blocks translucent and have colour similar as teeth. The block is ideal for crown and bridge usage given its advantage that does not required dipped in colouring for restorations. There is also no chipping for the cutting process using CAD/CAM machine. CEREC Zirconia also shows great biocompatibility with oral cavity and good mechanical properties for application. The wide range of usage of CEREC Zirconia in the current market makes it suitable as a commercial product to be compared with new emerging material.

Figure 2.4 CEREC Dental CAD/CAM Materials | Dentsply Sirona USA

From the user manual, CEREC Zirconia had a density of 6.08 ± 0.2 g cm^{-3}, high flexural strength (>900 MPa), bending strength of less than 900 MPa and grain size less than 0.4 µm. Chemical composition of CEREC Zirconia was listed in Table 2.3. Restorations made from CEREC Zirconia must be sintered in dry conditions and performed using sintering furnace. Table 2.4 shows the sintering protocol for CEREC Zirconia. After the sintering process, CEREC Zirconia was cooled down to room temperature before further processing.

Table 2.3 Chemical composition of CEREC Zirconia

Component	**CEREC Zirconia**
$ZrO_2 + HfO_2 + Y_2O_3$	≥ 99.0%
Y_2O_3	> 4.5 - ≤ 6.0%
HfO_2	≤ 5%
Al_2O_3	≤ 0.04%
Other oxides	≤ 1.1%

Table 2.4 Sintering protocol for CEREC Zirconia

Heating rate (°C/min)	Holding temperature (°C)	Holding time (min)
25	800	0
15	1510	120
30	200	0

Cokic *et al*., (2020) used CEREC Zirconia in their study to compare the performance with other zirconia ceramics. The study revealed that density of CEREC Zirconia had 6.06 ± 0.02 g/cm^3, and result from SEM microstructure analysis exhibited unimodal grain-size distribution with average grain size of 0.29 ± 0.12 µm (Cokic *et al*, 2020). Also, Cokic *et al*., (2020) found that CEREC Zirconia exhibited higher fracture toughness and flexural strength compared to Katana STML (3Y-TZP) zirconia ceramic. The average strength of CEREC Zirconia ranged between 917 ± 135 MPa. This study proved that CEREC Zirconia was a suitable reference for the tested materials.

2.9 Method of synthesis of nanometric zirconia stabilized oxide

Researchers have discovered different metal oxides such as yttria, calcium and magnesia have been used to stabilize zirconia by using various method such as sol-gel, hydrothermal, and co-precipitation method (Kwaśny & Balcerzak, 2017; Precious Ayanwale, 2018). The addition of transition metal oxides as stabilizer to the pure zirconia may obtain a multiphase material, which makes it completely or partially stabilized zirconia, hence reduce the impact of stresses that can lead to crack propagation (Hambire & Tripathi, 2013). Different methods greatly influence the properties of the material such as the particles sizes, shape and composition. Table 2.3 shows the ZrO_2 mixed metal oxide and their applications (Precious Ayanwale, 2018).

Table 2.5 ZrO_2 mixed metal oxide and their application (Precious Ayanwale, 2018)

ZrO_2 mixed metal oxide	Synthetic method	Application	Reference
ZrO_2 / ZnO	Sol-gel	Optical uses	(Bashir *et al*, 2013)
Al_2O_2 / ZrO_2	Sol-gel	Catalytic uses	(Del Angel *et al*, 2012)
ZrO_2 / CeO_2	Sol-gel Co-precipitation	Photocatalytic uses	(Rossignol *et al*, 1999)
CeO_2 / ZrO_2	Sol-gel	Catalytic uses	(Thammachart *et al*, 2001)
ZrO_2 / CeO_2	Co-precipitation	Thermal application	(Arsent'ev *et al*, 2014)
MgO / ZrO_2	Co-precipitation	Antibacterial uses	(Kumar & Muthuchudarkodi, 2017)
CeO_2 / Sc_2O_3 / ZrO_2	Co-precipitation	Fuel cells	(Liu *et al*, 2010)

One of the earliest studies reported by Duwes *et al* on stabilization of zirconia using calcia (CaO) and magnesia (MgO) that involved simple mixing of zirconia and oxide and pressed at 10,000 lb/in^2 followed by sintering shown the ratio of 16 – 30 mol% are required to stabilize using calcium, exhibited different crystallinity upon heating, while zirconia stabilized using 16 – 25 mol% of magnesia appeared in the form of cubic and monoclinic phases (Duwez *et al*, 1952).

Solvothermal synthetic route is an example of hydrothermal method which is employed to prepare a variety of nanomaterials by dispersing the starting material in a suitable solvent and then subjected to moderately high temperature and pressure conditions which lead to the formation of nanoparticles. When water is used as the solvent of the reaction, the method is called hydrothermal synthesis. Chemical parameters (example type, composition and concentration) and thermodynamic parameter (example temperature, pressure and reaction time) plays a unique part in the formation of the nanoparticles (Precious Ayanwale, 2018). Ceria-zirconia mixed oxide was prepared by hydrothermal synthesis, and it was reported that the size of the particles formed depends on the temperature used (Goto, 2015). Other than that, Wang *et al.*,

(2013) investigated the photocatalytic activity in visible light region ZrO_2-CeO_2 by the calcinated the precursor. From the studies, ZrO_2-CeO_2 showed an enhancement in photocatalytic activity when compared to the monocomponent of ZrO_2 and CeO_2 (Wang *et al,* 2013).

Co-precipitation method is a conventional method for the preparation of nanocrystals, which involves precipitating the oxo-hydroxide form from a solution of a salt precursor (example chlorides and nitrates metal salts) in a solvent (example H_2O or NaOH) by using a precipitating medium. The reaction condition and substrates influence the particle's diameter. Co-precipitation has been used to synthesize Y-TZP, which involve yttrium nitrate and zirconyl nitrate prepared in aqueous solution, compacted and sintered. The result showed that Y-TZP powder have BET surface area between 10 to $56m^2g$ with different calcination temperature. The surface area of the prepared powder decreased with the increase of calcination temperature (Pandey & Biswas, 2014). Besides, ytrrium (III) oxide (Y_2O_3) mixed with zirconium oxychloride octahydrate ($ZrOCl_2$) and aluminum sulfate ($Al_2(SO_4)_3$) was prepared by co-precipitation method to develop Al_2O_3 doped YSZ (Xiao *et al,* 2018). From the study, TEM micrographs showed the ceramics powder in the nano range with average crystalline size about 14 nm, meanwhile the crystalline size decreased when the amount of the doped Al_2O_3 increased up to 4 wt.% (Xiao *et al,* 2018).

Another research from Diaz-Parralejo *et al* (2011) synthesized YSZ powder using sol-gel method, which involved mixing of the zirconium (IV) n-propoxide diluted in propanol, nitric acid as surfactant and Yttrium (III) acetate. This study used methanol (MeOH), ethanol (EtOH) and butanol (BuOH) as solvent. From the results, the YSZ powder prepared in EtOH exhibited low porosity with high BET surface area compared to YSZ power prepared in MeOH and BuOH. The average pore sizes of sample prepared using MeOH, EtOH and BuOH are 12.9 Å, 12.0 Å and 12.6 Å, respectively. Also, this study described the BET surface area of the samples decreased with increasing calcination temperature up to 300 °C (Diaz-Parralejo *et al*, 2011). Furthermore, Rajabbeigi *et al* (2004) synthesized YSZ powder using sol-gel method by mixing zirconium nitrate and yttrium nitrate in aqueous solution, which has shown the formation of crystalline oxide in XRD pattern (Rajabbeigi *et al*, 2004). Other study by Istrate *et al.*, (2016) successfully prepared the ZrO_2-Y_2O_3 and ZrO_2-CaO used as a ceramic biomaterial for new bone formation around implant. In that study, ZrO_2-CaO behaved superior to mechanical tests compared to ZrO_2-Y_2O_3, which makes it suitable for further research in order to use in medical field (Istrate *et al*, 2016). Sol-gel method has been used widely to synthesize various zirconia mixed metal oxide nanoparticles (Precious Ayanwale, 2018) due to highly controllable and cost-effective method for production of homogeneous (Thiagarajan *et al*, 2017).

2.10 Chemical composition

Chemical composition such as stabilizing agent is one of the important factors that influenced the properties of zirconia ceramics. Zirconia framework can be altered before sintering in order to achieve the properties and stabilize the zirconia phases. Besides, zirconia can be stained to attain an aesthetic and natural appearance for veneering of fixed partial dentures, since zirconia color is off white. However, there was no significant different in strength between coloured and uncoloured zirconia (Farsi *et al*, 2006). In order to stabilize the zirconia phases to delay the crack propagation, a chemical need to be added into zirconia. The chemical that is added is also known as a precipitating agent. The solid precipitate can be separated from the liquid by filtration, decantation or centrifuge. Xiao *et al* (2018) synthesized spherical nano sized Al_2O_3