Chapter I

Introduction and

Literature Review

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1.1 Dental Ceramics

Dental ceramics mainly cover porcelain, glasses, glass ceramics and highly crystalline structures. They have better mechanical, physical, chemical and thermal properties than the metals and polymers. The properties of ceramics are modified for specific dental applications by control of the amount and type of the components used. Ceramic materials are more resistant to corrosion than the metals and polymers and do not react with the acids, alkalis and liquids [Kelly J.R. *et al.* 1996]. Ceramic materials are also stable over a long period of time. Dental ceramics show good flexural strength and fracture toughness. One of the strongest ceramics, zirconium dioxides has flexural strength similar to that of steel.

1.2 History of Dental Ceramics

For the last several decades, ceramics have a great importance in the human cultures due to their unusual properties. At that time, craftsmen used rocks that could be shaped by tools and artifacts by a technique called flaking in which stone chips were fractured away from the rocks such as, flint, ignimbrite, lava, obsidian, quartz and silicified limestone [Anusavice K.J. 2003]. In approximately 700 B.C. animal bone and ivory from the hippopotamus or elephant were used for dental implant. Later, human teeth sold by the poor and teeth obtained from dead were used. However, dentists disliked these options [Anusavice K.J. 2003].

The first porcelain tooth material has been invented by a French dentist (de Chemant) in collaboration with French pharmacist (Duchateau) in 1789. This product was an improved

version of "mineral paste teeth" made in 1774 by Duchateauin England. The latter compound, however, has not been used for the individual teeth due to the absence of an efficient manner to attach the teeth to denture base material.

An improved version of the porcelain tooth has been developed using Ash in 1837. In 1844, Stockton further refined the design and the mass production of the porcelain denture teeth. In 1903, Dr. Charles Land introduced the first ceramic crowns to dentistry [MacCulloch W.T. 1968]. These crowns exhibited great aesthetics, but the main reason of the failure was its low flexural strength.

For the last 35 years, feldspathic porcelains have been used in metal-ceramic prostheses because they have strong chemical bonding [Barreto M.T. *et al.* 1980, Christensen G.J. 1986]. Fig. 1.1 shows a schematic illustration of a cross-section of the metal-ceramic crown. Feldspathic porcelains have low strength, therefore, are not reliable for making all ceramic crowns without a cast-metal core or metal-foil coping. In addition to this, shrinkage during firing causes significant discrepancies in fit and adaptation of margins [Mackert J.R. (a), *et al.* 1986].

Fig.1.1 a schematic image of metal ceramic crown [http//www.nobledental.com.au]

Two of the most significant developments are responsible for the long-standing excellent aesthetic performance and clinical survivability of metal-ceramic restorations. One is to control the sintering temperature and the thermal expansion [Malhotra M.L. 1989]. Second is good thermal and chemical compatibility between the feldspathic porcelains and the alloys. Vita Zahnfabrik has developed the first commercial porcelain 'Vita' in 1963. It has excellent aesthetic and thermal properties and also allows to be used safely with a variety of alloys [Mackert J.R. *et. al.* 1988].

In 1965, McLean and Hughes developed a dental aluminous core ceramics consisting of 40-50 wt% of Al_2O_3 and a glassy matrix. A significant improvement in the flexural strength (131 MPa) of porcelain crowns has been achieved in this material. McLean reported a low 5-year failure rate of 2% for anterior crowns but an unacceptably high failure rate of 15% when aluminous porcelain used for the molar crowns [McLean J.W. and Hughes T.H. 1965]. Furthermore, the substantial sintering shrinkage (15% to 20%) of the aluminous porcelain at high temperatures and use of a 20 to 25 mm thick platinum foil, excellent marginal adaptation has not achieved.

Adair and Grossman have suggested that controlled crystallization of glass can enhance the properties of all-ceramic systems. In the 1990s, a leucite-based glass-ceramic (IPS Empress) containing approximately 34 vol% leucite has been introduced [Mackert J.R. *et.al* 1996]. It has provided an excellent strength and marginal adaptation and did not require special crystallization treatment. In the late 1990's, a pressable glass ceramic containing (IPS Empress2) 70 vol% of lithium disilicate crystal having high fracture resistance has been introduced [Erpenstein H. *et al.* 2000]. The fracture toughness of IPS Empress2 glass ceramics is 33 MPa-m$^{1/2}$ which is 2.5 times greater than that of IPS Empress glass ceramic

(13 MPa-m$^{1/2}$). These improvements in the compositions of ceramics and method of forming have significantly enhanced the application of all-ceramic crowns with an excellent fracture resistance.

1.3 Ceramics for Dental restoration, why?

There is a long history of using ceramics in dental restorations due to their good esthetics and function as missing teeth [Denry I.L. 1996 (a), Kelly J.R. 2004]. In addition to this, ceramics have no effect on the health and also do not create any cytotoxicity. It can also survive the chewing forces that vary between 400 and 800 N. They also allowed the right balance and support between the bone and soft tissues. Ceramics are less mechanically authentic than the metals. At present, research is going on to improve the mechanical strength and toughness of the ceramics [Meriani S. 1989]. Most common uses of the ceramics are inlays, onlays, veneers crowns and structural replacement of a tooth. These all are thin layered structures which may be composed of metal-ceramic or all-ceramic materials. Some examples are depicted in Fig. 1.2.
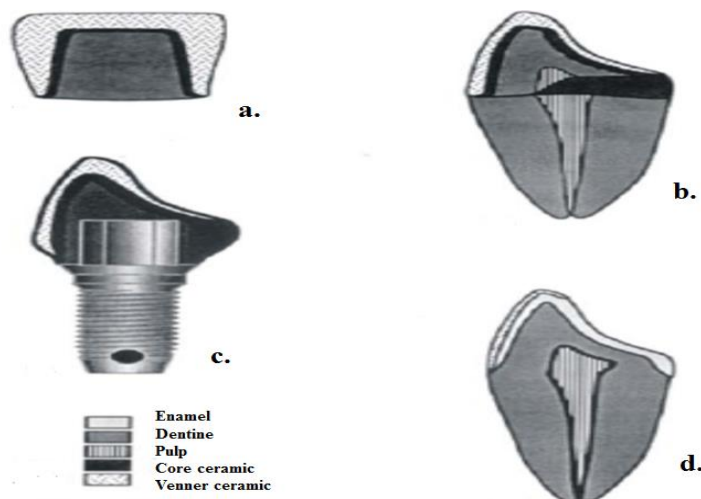

Fig. 1.2 Dental restorations (a) In-Ceram crown with the standard crown design. (b). Lateral view of In-Ceram crown demonstrating underlying tooth structures. (c) Lateral view of the ceramic crown on a titanium implant. d. Porcelain veneer resin bonded to tooth enamel [Narayan R. 2009]

Dental ceramics are classified into two categories; metal ceramics and all-ceramic systems. The metal-ceramic systems are feldspathic porcelains and all-ceramic consist of glass-ceramics, glass infiltrated ceramics and sintered all zirconia or alumina monolithic ceramic materials [Mackert J.R. *et al.* 2001, Holland W. *et al.* 2000]. They further subdivided into different categories by processing routes, uses, microstructure, aesthetic signature and mechanical properties. Table.1.1 shows the different categories and mechanical properties of the dental ceramics.

Table. 1.1 Dental materials and their strength

Materials		Flexural strength (MPa)
Porcelains	Feldspathic	60-100
	Leucite	120-180
Glass ceramics	Lab cast/cerammed	115-125
	Premade/HIP	140-220
Glass infiltrated	In-ceram alumina	400-600
	In-ceram spinel	325-410
	In-ceram zirconia	700-800
Monolithic ceramics	Lava Y-TZP	1000-1200
Tooth structures	Procera	500-600
	Dentine	16-20
	Enamel	65-75

1.4. Metal-Ceramic Restorations

It is a fixed restoration that employs a metal substructure on which a ceramic veneer is fused. The feldspathic porcelains are mostly preferred for metal-ceramic restoration [Christensen G.J. 1986, Mackert J.R. (b) *et al.* 1986]. The compositions are based on SiO_2-Al_2O_3-K_2O ternary system. Specifically, SiO_2 and potash feldspar ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$) are the basis for dental porcelains. Other additives such as opacifiers (TiO_2, ZrO_2, and SnO_2), suitable, appropriate pigments and fluxes (to reduce the melting point) were also added [Mackert J.R. *et al.* 1988]. The porcelains were normally classified regarding their firing temperatures: high temperature (1300 °C), medium temperature (1100–1300 °C), low temperature (850–1100 °C) and ultra-low firing (<850 °C). Leucite ($KAlSi_2O_6$) is the most important aspect of the development of feldspathic porcelain [Mackert J.R. and Evans A.L. 1991]. The presence of leucite increases the coefficient of thermal expansion of porcelains to the extent that makes a good bonding between the porcelain and metal substructure [Anusavice K.J. and Gray A.E. 1989]. The flexural strengths of feldspathic porcelains are quite low (60-100 MPa). The flexural strength, however, increases to 300 MPa when bonded with the metal substructure [Anusavice K.J. and Gray A.E 1989].

1.5 All-Ceramic Restorations

This type of restoration consists of a composite of the glass, ceramic and they are processed into a complex shape using a glass shaping technology. These materials are also referred to as castable/pressable glass-ceramics [Heintze S.D. *et al.* 2008]. The ceramic particulates are formed in a glassy matrix by nucleating and growing the ceramic crystals with suitable heat treatments (also known as ceramming). The first glass ceramic developed by Dicor R consists of a magnesium aluminosilicate glass and 45% of fluromica ($K_2Mg_5Si_8O_2F_4$)

crystals. Dicor R materials do not have the ability to attain the interior color. Another outstanding glass ceramic is Empress 1Ressentially a leucite-reinforced feldspathic porcelain. The controlled nucleation of leucite enhances the mechanical properties. The flexural strength of Empress 1R is the same as that of DicorR. The translucency of this material is slightly less than Dicor R but can be managed in the restorations.

Another glass ceramic is Empress 2R consisting lithium silicate based system. Its microstructure is very dense having 70% of elongated lithium-disilicate crystals by a proper composition choice and the heat treatment [Kelly J.R. *et al.* 1991]. The manufacturer recommends the use of this material for inlays, onlays, veneers, etc.

Monolithic ceramics are an example of this type of material. It contained 99.9% alumina and sintered at 1600 °C to produce a core compatible with the dental porcelain. The mechanical strength is good, but the high sintering temperature causes a substantial shrinkage. A CAD-CAM system is used to obtain high dimensional tolerance. Once the sintered coping is obtained, matched porcelain is placed on the coping. Furthermore, this material is limited to be used as a single unit restoration in the anterior or posterior regions.

The monolithic ceramics have been further modified by introduction of the toughened zirconia specifically yttria-tetragonal zirconia polycrystals (Y-TZPs) [Heuer A.H. and Hobbs L.W. 1981, Meriani S. 1989]. The doping of yttria in zirconia results in a metastable tetragonal phase. During the propagation of a crack, the tetragonal phase transforms to the monoclinic phase. This dissipates the energy from the propagating crack. This further increases the strength as well as the toughness of monolithic zirconia twice that of monolithic alumina. There are several dopants such as CaO, MgO, and CeO_2 that can produce most esthetically pleasing restoration. CeO_2 doping can produce even better

mechanical properties, but it has its unique color. The most interesting aspect of Y-TZP is its high mechanical strength therefore can be machined in Lava CAD/CAM system to produce the complex bridges [Denry I. and Kelly J.R. 2008].

Glass-infiltrated ceramics – these materials are based on partially sintered alumina, spinel, and zirconia commercially known as In-Ceram Spinel R, In-Ceram Alumina R, and In-Ceram Zirconia R [Estafan D. *et al.* 1999, Sohmura T. and Takahashi J. 1995]. They have surface pores, infiltrated with the lanthanum aluminosilicate glass. The addition of lanthanum decreases the viscosity of silicate melts which supports in infiltration and simultaneously improves the strength of the ceramic core. The mechanical properties of In-Ceram R materials are better than the other restorations. In-Ceram R materials are opaque and easily stained too [Giordano R. 2000].

1.6 Clinical Failure of All-Ceramic Crowns

In spite, the wide variety of all-ceramic restorative materials, they are still not highly recommended by dentist [Pospiech P. 2002]. For, e.g., Dicore ceramic crowns luted with Zn-phosphate cement have been reported to show poorer success rates than the crowns cemented and bonded with composite resin cement. Internal surfaces have the highest tensile stresses and critical flaws. Etching and polymer coating of tensile surfaces can increase the strength of these ceramic materials by blunting the crack tip or by reducing the stress corrosion by barrier coatings [Kelly J.R. *et al.* 1989, 1990].

1.7 Components of metal ceramic restoration

A metal-ceramic crown composed of a metal substructure and a porcelain veneer. A surface oxide layer lies between the metal substructure and veneer is considered as a separate

component. Porcelain veneer has three layers, an opaque, dentin, enamel, and a surface glaze.

1.7.1 Metal substructure

Low fusing dental porcelain has the less strength. Therefore, a metal substructure is needed to support the porcelain veneer [Ozcan M. and Niedermeier W. 2002]. The thickness of the metal coping depends on the casting alloy used and the amount of tooth structure reduced by the dentist.

1.7.2 Oxide layer

The metal oxides that forms on the surface of the alloys during heat treatment plays a major role in bonding the dental porcelain to the metal substructure. The chemical nature of this oxide film depends on the alloy's composition.

1.7.3 Opaque layer

The opaque layer serves three major functions to establish the porcelain-metal bond, to mask the dark color of the metal substructure and to initiate the development of selected shade of the porcelain [Barghi N. and Lorenzana R.E. 1982]. The dimension of this layer varies among different brand of the dental porcelain and color of oxidized metal substructure to which it is applied [Christensen G.J. 2009]. The thickness of this layer lies between 0.2 to 0.3 mm. All the opaque layers are vacuum fired on the metal substructure in a dental porcelain furnace [Kurklu D. *et al.* 2013].

1.7.4 Dentin porcelain layer

It is the initial layer of dental porcelain that imparts the color. The dentin layer is overbuilt slightly during the fabrication process, cut back, and overlaid with the enamel porcelain in that section of the restoration where the higher translucency is required [Munck J.D. *et al.*

2004]. The combined thickness of the fired dentin and enamel layers is in the range 0.5-2.0 mm. If the thickness is more than 2 mm, then it would be unsupported by the metal and more prone to fracture.

1.7.5 Enamel porcelain layer

It is an enamel powder and used where the natural translucency is desired. Enamel porcelains are employed in the incisal and interproximal areas [Hussam M. *et al.* 2014]. Enamel layer is overlaid on the dentine layer and co-fired in the vacuum furnace.

1.7.6 External glaze

The exterior glaze is applied on the outer surface of the dental porcelain to create a natural luster. After implementing the glaze on the porcelain's surface, fired it at a certain temperature for a fixed time until a natural luster is achieved.

1.8 Classification of dental porcelains

Dental porcelains are classified according to their chemical composition and use. All feldspathic porcelains are not used for bonding to the metal substructure. The feldspar forms a glassy matrix to which other ingredients are added gives different types of the porcelains for various applications [Derand P and Peter V. 1999]. The feldspathic porcelains are classified into three categories:

- High fusing: 1288 to 1,371 °C.

- Medium fusing: 1093 to 1,260 °C.

- Low fusing: 871 to 1066 °C.

High and medium fusing porcelains have the same chemical compositions and the morphology. They are applicable in the denture teeth. Low fusing porcelains are used in

metal, ceramic restoration. It has the different composition to that of high and medium fusing porcelains.

1.9 Chemical components of dental porcelain

The main components of the dental porcelain are feldspar, quartz, alumina and kaolin in the glassy matrix. The details are given below:

1.9.1 Feldspar ($K_2O\ Al_2O_3 6SiO_2$)

Potassium, sodium and calcium feldspar are the naturally occurring minerals. Feldspars are used in the preparation of different types of dental porcelain for application in the metal-ceramic and other glass-ceramics [Rouf M.A. 1978]. The main property of the feldspar is that it melts incongruently when heated in the temperature range 1150 ℃ to 1530 ℃. It forms a crystalline leucite and the glassy matrix. Leucite is a potassium-aluminum-silicate component having high CTE $20\text{-}25 \times 10^{-6}$ /℃ [Cattell M.J *et al.* 2005]. This tendency of feldspar to form leucite during incongruent melting is used in the porcelain for metal bonding.

1.9.2 Quartz (SiO_2)

Quartz has a high fusion temperature and serves as a framework for other ingredients. It also provides the strength to the porcelain [Noni A. D. *et al.* 2009].

1.9.3 Alumina (Al_2O_3)

Alumina is one of the components of the dental porcelain. Its coefficient of thermal expansion is similar to that of low fusing porcelain. Alumina has a slight solubility in low-fusing porcelain and improves the overall strength. It also increases the viscosity of the melt (Steyern V.V.P. 2005, Al-Sanabani F.A. *et al.* 2014).

1.9.4 Kaolin (Al_2O_3-$2SiO_2$.$2H_2O$)

The addition of kaolin to the unfired dental porcelain increases its moldability. It is added in a minuscule quantity due to its opaqueness to maintain the translucency of the porcelain [Hashimoto S. *et al.* 2005].

1.10 Verities of low fusing porcelain for metal-ceramic restoration

There are different brands of the low fusing porcelains and they differ regarding the composition, particle size distribution, aesthetics, handling, shrinkage and the cost. Traditional porcelain has opaque porcelains, dentine and enamel body, modifiers, stains and glazes as major components. The formulations of these components will vary in the different brands of the porcelain.

1.10.1 Opaque porcelains

These porcelains are made by the addition of insoluble oxides for e.g. SnO_2, TiO_2, ZrO_2, CeO_2, $ZrSiO_4$, BaO, ZnO and Rb_2O. These oxides have high refractive index and therefore, scatter light. The opaque powder contains 8 to 15% of the metal oxides and some of the particles are less than 5µ. Particle size distribution influences the opaque's ability to mask the color of metal substructure [Davis B.K. *et al.* 1990]. The masking ability of the opaque powder can be further influenced by the amount and color of the oxidized metal casting [El-Meliegy E.A.M. 2004]. The thickness of an opaque layer is differed among the brands of the porcelain and varies for different shades within the same porcelain system [Fredericci C. *et al.* 2011]. The thickness ranges from 0.2 to 0.5 mm. The opaque should be applied properly on the metal substructure to obtain a uniform thickness. The color shade can be further modified by adding the stains.

1.10.2 Dentine porcelains

These porcelains are the major determinant of the metal-ceramic restoration. In porcelain kits, dentine exists in the different shades. However, for every dentine shades, same enamel and translucent powders may be used [Tsetsekou A. *et al.* 2002]. Dentine porcelains are used in the areas of restoration other than the gingival one-half of a crown. In natural looking restoration, dentine porcelains are needed to extend the incisal one-third or occlusal surface to underlie enamel covered incisal edges [Cheung K.C. and Darvell B.W. 2002].

1.10.3 Enamel porcelains

These porcelains are referred to as incisal porcelains. It is not restricted to any particular area of the tooth even it can be used in the gingival one-half to the gingival one-third of a porcelain buildup [Stacey G.D. 1993]. Enamel porcelains are more translucent than dentine porcelain. They are available in the insufficient range and the shades are usually in the violet to gray range. Only four to five bottles of enamel powders are available in any porcelain kit to cover the entire range of the shades.

1.10.4 Translucent porcelains

Translucent powders do not allow the transmission of all the light. These are applied on the whole surface of the porcelain buildup. Translucent porcelains impart depth and natural enamel-like translucency without affecting the shade of the body.

1.10.5 Modifiers

These porcelains are highly color concentrated and used in achieving the internal color modifications. All the dentine, enamel, translucent and body modifiers have the same composition and physical properties. They differ only in appearance because of the amount and type of the pigments they contain [Anusavice K.J. 2003]. However, modifiers are color

intense; dentine is color predominant and enamel, translucent are the color reduced. Some of the coloring oxides are given below:

- **Yellow:** Indium, praseodymium (lemon), vanadium, zirconium or SnO_2 diluted with chromium.

- **Green:** Developed from chromium oxide but avoided in dental porcelain because it has the characteristic color of glass.

- **Pink:** Derived either from chromium-tin or chrome-alumina. However, stable up to 1350 ºC, therefore, used only in low fusing porcelains.

- **White:** CeO_2, TiO_2, ZrO_2.

- **Black:** Fe_2O_3

- **Gray:** Produced from platinum gray or by diluting iron oxide.

- **Blue:** Obtained from cobalt salts.

1.10.6 Stains and glazes

Stains are the mixture of metallic oxides and low fusing glasses. The fusion point should be less than that of the maturing temperature of the dentine and enamel. These stains allow developing surface characterization and color modification for custom shade matching [Yilmaz B. *et al.* 2012]. They contain less silica and alumina and more sodium and potassium oxides and also some colorant oxides. Glazes are colorless low fusing porcelain and possess fluidity at high temperature. A glazed body has a less surface porosity and appears glossy after firing. The stains and glazes, however, do not provide optical qualities. They are only for appearance and refract light for internal color modifications veneered by either dentine or enamel [Ozcelik T.B. *et al.* 2008].

1.11 Porcelain and glass-ceramic application on metals

The porcelains are in the form of powder for ceramic and metal ceramic prostheses. They are mixed either with water or other liquid for application. The particles should be of different sizes to achieve dense morphology. The size of the starting powder particles influences not only the degree of condensation of the porcelain but also the soundness or apparent density of the final product. Dense packing will lead to a lower firing shrinkage and less porosity after firing. Porcelain on the metal substructure can be applied using various techniques for, e.g., vibration, spatulation, and brush techniques.

In mild vibration technique, the wet powder is densely packed on the underlying framework by vibration and the extra water is wiped away using a tissue or a fine brush. In spatulation technique, the wet powder is spread over the framework and smoothed using a spatula. The excess water accumulates on the surface during smoothing which can be removed using a tissue. The third method employs the addition of dry porcelain powder to the surface to absorb the water. A brush places the dry powder to the side opposite from an increment of wet porcelain. As the water is drawn toward the dry powder, the wet particles are pulled together. The driving force for the packing or condensation is the surface tension in all the techniques.

1.12 Heat treatment of dental porcelain

The heat treatment is necessary to sinter the particles of powder to form the prosthesis. The chemical reactions occur during prolonged firing time. Leucite content present in the dental porcelains is responsible for the thermal changes in it. Leucite is a high thermal expansion crystalline material. Therefore, it significantly affects the thermal expansion of the porcelain [Fischer J. *et al.* 2009]. Thermal expansion coefficients of the porcelains and

metal can be matched by varying the amount of leucite content in the porcelain [Zhang Y. *et al.* 2008]. Different thermal processing histories resulted in the different cooling rates with concomitant variation in the thermal expansion coefficients [Mackert J.R. *et al.* 1995]. The various heat treatments can also lead to cracking of the porcelains due to the thermal mismatch [Holland W. *et al.* 2000]. Microcracking may also take place due to the phase transition from cubic to tetragonal upon cooling. Leucite content in commercial porcelain increases from 6 to 21 vol% after an isothermal hold at 750 °C for 4-16 min (simulating post-soldering treatment). The leucite content increased from 11 vol% to 56 vol% after slow cooling [Mackert J.R. *et al.* 2001].

The condensed porcelain mass is placed in the muffle of a preheated furnace at approximately 500 to 550 ºC for low-fusing porcelain. The preheating leads to evaporation of the extra water. Direct placement of the condensed mass into a warm furnace may results in a crack due to the rapid evolution of the vapor. After preheating for approximately 5 min, the porcelain is placed into the furnace and the firing cycle is initiated. During the heat treatment, initially, the porcelain particles bond at their points of contact. As the temperature is raised, the sintered glass gradually flows to fill up the air spaces in the voids. However, air trapped in the form of voids because the fused mass is too viscous to allow all the air to escape. A vacuum firing may reduce the porosity in the porcelain. The powder particles inside the furnace are packed together with the air channels around them. As the air pressure inside the furnace is reduced about one tenth of atmospheric pressure by the vacuum pump the air around the particles is also reduced. The closed pores are formed within the condensed porcelain during heat treatment. The air inside the closed pores is isolated from the furnace atmosphere. At a temperature about 55 ºC, the vacuum is released

and the pressure inside the furnace increases from 0.1 to 1 atm. Due to increase in pressure, the voids are compressed to one-tenth of their original size consequently the total volume of porosity is reduced. However, a few bubbles are still present in vacuum heat treated porcelains, but they are markedly smaller than the ones obtained in the conventional heating.

1.13 Advantages and disadvantage of metal ceramics restoration

The most notable benefits of metal-ceramic prostheses are their good aesthetic quality and high resistance to fracture. There is almost no wear of the porcelain occurs by abrasion and staining along the interface between the metal and veneer. It has also been clinically proved that its fracture rate is very less 2.1% after 7.5 years [Coornaert J. *et al.* 1984]. In addition to this, metal ceramic prosthesis needs less tooth structure to be removed to provide the proper bulk for the crown. Due to these, metal ceramics restoration is the most widely used prosthesis system in fixed prosthodontics today.

The major disadvantage of the fixed metal ceramic restoration is the accumulation of the secondary carries in the marginal gap [Goudouri O.M. *et al.* 2014]. It is also associated with plaque accumulation around marginal discrepancies and open marginal configuration of the fixed dental prostheses. This leads to a bacterial attack and dissolution of the luting cement [Bergenholtz G. *et al.* 1982].

1.14 Dental ceramics for PFM bonding

The metal ceramic restoration consists of a metal frame supporting the ceramic materials which are chemically and mechanically bound. On these days, porcelains are widely used

in the dentistry due to their low cost and some unusual properties e.g., color, strength, aesthetic, opacity, translucency, durability etc. [Mrazova M. and Klouzkova A. 2009]. Before the 1960s, the conventional dental porcelain having a maturing temperature of 1000-1300 ℃ fused on platinum alloys of iridium or ruthenium were used. However, the product is highly liable to fracture. Therefore, the use of dental porcelains was limited to an aesthetic one in the interior teeth. In addition to this, these porcelains have a low value of the coefficient of thermal expansion (CTE) 8×10^{-6} /K which creates the problem of bonding it to the metal framework. In 1962, Weinstein developed the porcelain of CTE 17×10^{-6} /K using the glass and glass ceramic frits of different composition and CTE. In 1964, Briand et al. mentioned that the leucite is a major component of the dental porcelain. Tetragonal leucite is reported as a critical component in glass-ceramics for better thermal expansion matching [Brodkin D. and Panzera C. 2000]. Its presence in the dental porcelain increases the strength, durability, and translucency of the final product [Denry I.L (b). *et al.* 1996]. The major advantage of using glass ceramics containing tetragonal leucite is that the leucite has the same refractive index as the glass. Therefore, translucency is never hindered by the crystallization of the leucite in a glass.

Becerro et al. reported that kalsilite mineral ($KAlSiO_4$) having a high CTE could be used for PFM bonding [Becerro A.I. (b) *et al.* 2009]. Kalsilite has a framework of aluminum silicates containing a network of tetrahedral Si and Al elements with alkali metal ions, occupying tetrahedral and octahedral sites to counterbalance the charge valency. Kalsilite has also studied as the precursor of leucite, which is a major component in porcelain-fused-to-metal (PFM). Thermal expansion coefficient of kalsilite is 16×10^{-6} /°C [Ota T. et al. 1996].

1.15 Mechanochemical synthesis

In mechanochemical synthesis, the powders are prepared by high energy ball milling of the elemental mixtures also referred to as mechanosynthesis, mechanical driven synthesis, mechanical alloying and high energy milling. In this synthesis, chemical reactions occur at the interfaces of the nanosized particles that are continuously regenerated during milling [Takuya T. and Paul G.M. 2004]. The other possibility is the occurrence of the reaction by a self-propagating process at high temperature. For the self-propagating process, a source of energy must be available to raise the adiabatic temperature of the system to that required for it to become self-sustaining. The high surface energy of very fine powders is quite enormous. For e.g., the starting average particle size of Mo and Si powders before the formation of the $MoSi_2$ have been reported as ~20 nm and ~ 10 nm respectively [Rahaman M.N. 2003].

The milling of the powders can be carried out in small mills such as Spex mill for small quantity or Attrition mills for larger quantities employing a cylindrical jar containing milling balls as a grinding media. The milling time is usually few tens of hours. Mechanochemical synthesis has some advantages over the others synthesis routes regarding the low cost, fine particle size, low agglomeration, narrow size distribution, and uniformity of crystal structure and morphology [Takuya T. and Paul G.M. 2004]. One more advantage of this method is the ease of preparation of powders such as silicides and carbides that can otherwise be difficult to produce. Authors have been reported the mechanochemical technique is superior to both the conventional solid-state reaction and the wet-chemistry-based processing routes for the ceramic powders. It uses low-cost and widely available oxides as the starting materials [Xue J. *et al.* 1999]. Furthermore, the mechanically derived

powders possess a much higher sinterability than those powders synthesized by the conventional solid-state reaction and most of the wet chemical processes [Kong L.B. *et al.* 2002]. A disadvantage is the incorporation of the impurity from the milling media into powder.

1.16 Leucite ($K_2O\ Al_2O_3\ 2SiO_2$)

Leucite ($KAlSi_2O_6$) is a potassium aluminosilicate mineral phase having a (Si, Al)O_4 tetrahedra (Fig.1.3), each of which shares all its oxygen with its neighbors [Denry I.L. (c) *et al.* 1996]. It exists in two polymorphs, a cubic phase, and a tetragonal phase. Cubic phase is the high-temperature phase and it transforms to tetragonal phase while cooling to 500-600 ºC [Brodkin D. and Panzera C. 1999].
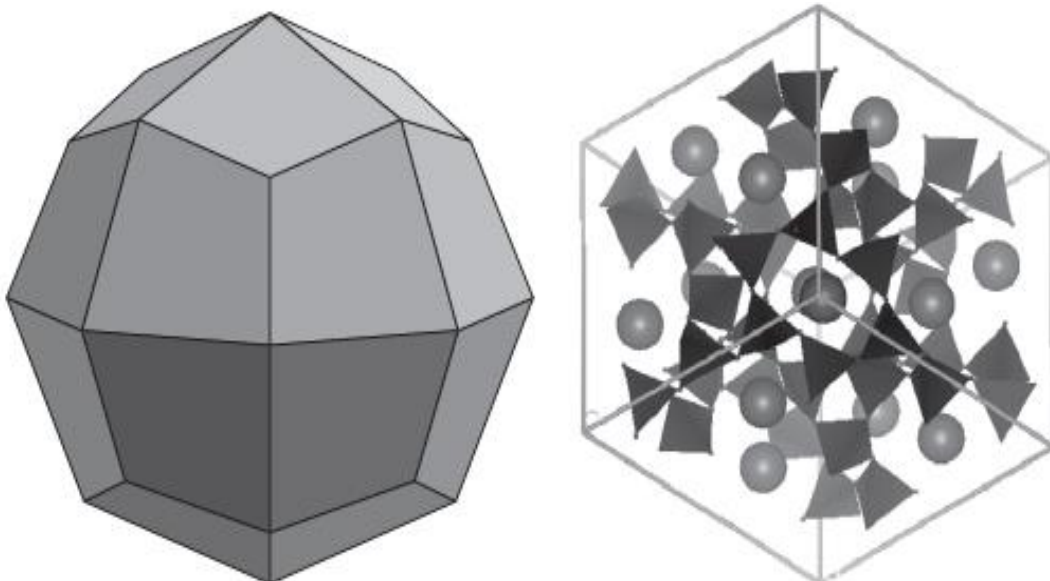

Fig. 1.3 Single leucite crystal (left) and Crystal structure of tetragonal leucite (right); spheres-K$^+$ ions, tetrahedral-[SiO$_4$]$^{4-}$.[AlO$_4$]$^{5-}$

This transformation is rapid, reversible and continuous. The elementary unit cell has 48 tetrahedra and 16 potassium cations. The potassium ions are too small to fill the cavities in

the cubic structure and moved from their positions at lower temperatures. Leucite crystallizes incongruently from a precursor containing potassium, alumina, silica and other components like alkali fluxes, nucleating agents, etc. Some nucleating agents (P_2O_5, MgO, CaO, ZrO_2, ZnO TiO_2) are added to initiate the incongruent crystallization of the leucite at a lower temperature.

1.16.1 Synthesis of leucite glass-ceramics

Leucite glass-ceramic is the most widely used dental ceramic for all the type of metal alloys for application in coping. It provides high CTE ($20\text{-}27\times10^{-6}$/°C), high strength, color appeal, suitable refractive index and good biocompatibility [Mackert J.R. *et al.* 2001, Mrazova M. and Klouzkova A. 2009]. Leucite enhances the CTE of glass-ceramic to make it thermally compatible with the metal. Pure leucite phase has a high melting point 1693 °C [Zhang Y (a). *et al.* 2007, Meliegy E.E. 2012]. This phase is partially obtained, when potash feldspar melts incongruently in the temperature range 1120-1150 °C. The presence of natural impurities in the feldspar is the main drawback. These impurities may discolor the glass-ceramics or undesirable color may be produced. The traditional method for manufacturing feldspathic dental glass-ceramic is to make glass frits and subsequent heat treatments for crystal growth. The leucite ceramic contains leucite crystals with a particle size about 10 μm have been successfully used in the dental restoration [Zhang Y. *et al.* 2008]. Leucite volume fraction in commercially available dental porcelain typically ranges between 17 to 45 wt. % in a low-temperature frit matrix [Mackert J.R. (b) *et al.* 1986]. Leucite crystallizes by the heat treatment of a precursor glass containing K_2O, Al_2O_3, and SiO_2 and other components like alkali fluxes, nucleating agents and grain growth inhibitors. The obtained glass ceramics contains less than 40 vol% tetragonal leucite and a residual

glass matrix. Leucite can also be crystallized using aluminosilicates glass [Yilmaz H. and Dincer C. 1999]. The crystallization, however, occurs via uncontrolled nucleation leads to different crystals sizes and irregular microstructure. The glass ceramic with a high content of leucite crystals has also been prepared using solid state sintering [Ota T. *et al.* 1993, Wolfram H. *et al.* 1995], salt-bath [Oishi S. *et al.* 2003], co-precipitation, [Sheu T.S. *et al.* 1994], sol–gel [Zhang Y (b). *et al.* 2007] and hydrothermal [Novotna M. *et al.* 2004] synthesis processes. Though several methods have synthesized leucite glass-ceramic, the synthesis of pure, complete crystalline leucite powder below 900 °C has never been reported, as it is always accompanied by a glassy phase [Levin E.M. *et al.* 1964].

Jankeviciute et al. have been synthesized leucite at 950 °C via sol-gel derived molecular precursor [Jankeviciute A. and Kareiva A. 2011]. Sheu et al. have been prepared the leucite powder using co-precipitation method followed by sintering at 1200 °C [Sheu T.S. *et al.* 1994]. Zhang et al. synthesized the high purity leucite powder at 850 °C via sol-gel method by using 1.5 wt.% of CaF_2 as a modifier [Zhang Y. *et al.* 2006]. They suggested that the addition of CaF_2 not only lowers the synthesis temperature but also provides the pure and fine grained leucite which is beneficial to the mechanical properties for PFM. Cattell et al. have been prepared the leucite glass-ceramics for the dental applications by traditional melt quench method followed by heat treatment at 1250 °C [Cattell M.J. *et al.* 2005]. Hashimoto et al. have been investigated the conventional thermal processing of leucite using $Al_2(SO_4)_3$, kaolin and K_2SO_4 (3:3:15) as the starting materials and heat treated at different temperatures (850-1100 °C). They have observed the formation of pure leucite at 1100 °C without any impurity phase.

Yao et al. have been prepared a superfine leucite-reinforced dental material by heat-treating the mixture of hydrothermally derived leucite precursor and low-temperature frit at 750 °C [Yao L. *et al*. 2011]. They suggested that the uniform distribution of ultra-fine leucite crystals in PFM is beneficial for improving the mechanical strength, wear resistance, toughness, and densification of the dental porcelain [Denry I.L. (b) *et al.* 1996, Masayuki K. *et al.* 1994].

There is no work has been reported on the synthesis of leucite using mechanochemical synthesis route. The mechanochemical process is a chemical reaction induced by a self-propagating process during milling, resulting in lowering of calcination and sintering temperature [Saito F. *et al* .2004]. The source of energy for the reaction is the stored strain energy of the fine powder particles. This synthesis route is a simple, economical and also a suitable method for large-scale production of nanopowders [Ding J. *et al.* 1996]. This process has also been successfully used to obtain the nanoparticles including Al_2O_3, ZnO, $SrAl_2O_4$, ZrO_2, $BaTiO_3$ and $BaAl_2O_4$ [Chen G. *et al.* 2005, Kong L.B. *et al.* 2002].

1.17 Kalsilite (K_2O Al_2O_3 SiO_2)

Kalsilite ($KAlSiO_4$) is a silicate mineral [Ota T. *et al.* 1996]. It has a framework of alumina silicates containing a network of tetrahedral Si and Al elements with charge balancing alkali metal ions [Andou Y. and Kawahara A., 1984]. The crystal structure of kalsilite is derived from the tridymite by rotating the tetrahedral in the (001) plane and it has the space group $P6_3$. The Si and Al atoms are arranged tetrahedral distances (T-O), 1.61 & 1.74 Å.

```
┌─────────────────────────────┐
│ Disordered high-kalsilite   ├──────── P6₃/mmc
└─────────────────────────────┘
                                              │
                                              │ t2
                                              ↓
      ┌──────────────────┐
      │ High-kalsilite   ├─────────────── P6₃mc
      └──────────────────┘
                                              │
                                              │ t2
                                              ↓
      ┌──────────────────┐
      │ Low-kalsilite    ├─────────────── P6₃
      └──────────────────┘
```
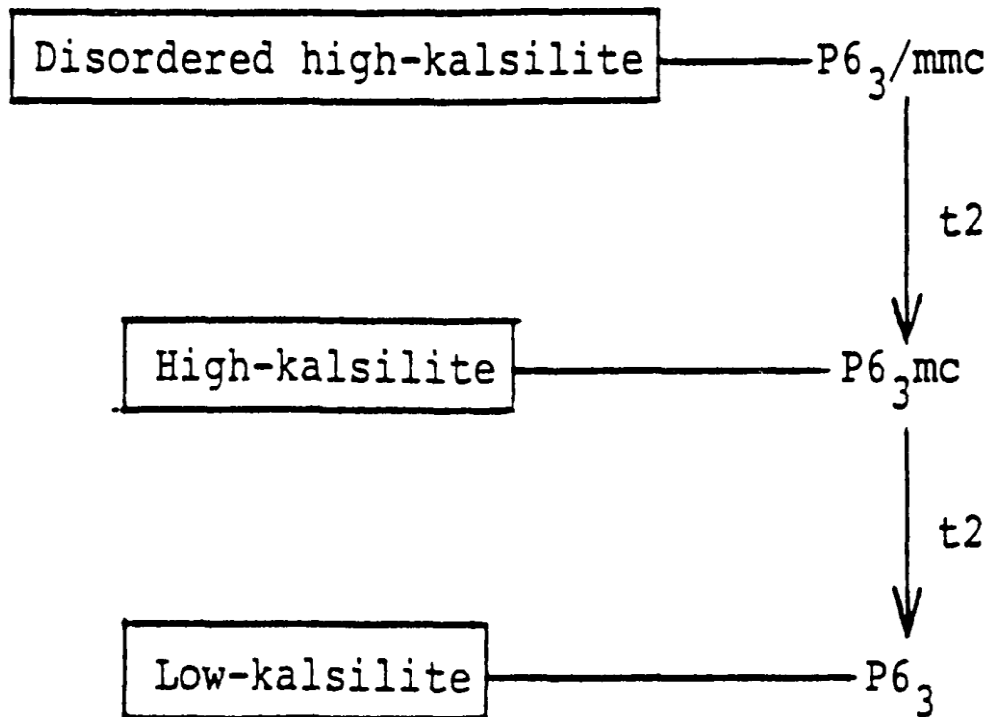
Fig. 1.4 The relationship among three polymorphs of the kalsilite [Kawahara et al. 13, (1987) 260-270]

Oxygen atoms are connecting Si-Al tetrahedral and occupy three-fold positions displaced by 0.25 Å from the ideal position on a triad axis. The bond angles of T-O-T decreases to 163º. Kalsilite exists in three polymorphs and it undergoes a phase transformation at 865 ºC having the space group $P6_3mc$ [Kawahara A. *et al.* 1987]. Fig. 1.4 shows the subgroup relationship between the three polymorphs of the kalsilite. It has three kinds of symmetries, topological symmetry ($P6_3/mmc$), topochemical symmetry ($P6_3mc$) and real symmetry ($P6_3$). The kalsilite has a hexagonal crystal structure having space group $P6_3mc$ with a = b = 5.30 Å and c = 8.65 Å [Perrotta A.J. and Smith J.V 1965].

1.17.1 Synthesis of Kalsilite

Kalsilite is a significant constituent in PFM and ceramic restoration systems. It is used as the precursor of leucite [Becerro A.I. (a) *et al.* 2009]. Becerro et al. has previously reported that kalsilite is a high thermal expansion ceramic for bonding to metals. Kalsilite, however, crystallized as a metastable intermediate phase when synthesizing leucite [Zhang Y. (b) *et al.* 2007]. It has been synthesized previously by various techniques such as; hydrothermal synthesis [Kopp O.C. *et al.* 1961], sol–gel synthesis [Bogdanoviciene I. *et al.* 2008] and solid-state method [Kallai L.H. and Lapides I. 2003]. Becerro et al. have suggested a simple and economical technique synthesize the kalisilite from a precursor of kaolinite using hydrothermal synthesis route [Becerro A.I. (b) *et al.* 2009]. Bogdanoviciene et al. have been synthesized kalsilite using sol-gel route at 750 ℃. They suggested that the crystallinity of the sample slightly depends on the chemical composition and temperature of the annealing [Bogdanoviciene I. *et al.* 2007]. Amongst other synthesis methods, mechanochemical synthesis is an economical and suitable method to prepare the pure materials with a microfine particle size [Dimitrijevic R. and Dondur V. 1995, Lianshui S. *et al.* 2014, Balaz P. *et al.* 2013]. There is a lack of research in the stabilization and implementation of the kalsilite as PFM. Further, no work has been reported on synthesis of kalsilite using the mechanochemical route.

1.18 Bioactive Glasses

Bioactive glasses have bioactivity and the biocompatibility and are used as highly effective implant materials in the human body to replace or repair the damaged tissue. Bioactive glasses are widely used in musculoskeletal applications, a smaller subgroup of dentistry. Bioactive glasses are derived from a Na_2O-CaO-P_2O_5-SiO_2 ternary system with other

substitutions [Hench L.L. 1998]. Unlike soda lime glasses, it contains less SiO_2 and high Na_2O and CaO. Due to this, its surface is highly reactive when exposed to the body fluid. The most commercially important composition is 45S5 containing 45 mol% SiO_2.

Lopez-Esteban et al. modified the original compositions of the bioactive glass to make them compatible to the metallic implants regarding the coefficient of thermal expansion [Lopez-Esteban S. *et al.* 2003]. In which, Na_2O and CaO were partially substituted by K_2O and MgO respectively. This results in thermal expansion coefficients compatible to metallic implants. The processing of such glasses can be performed by the traditional glass melting process or by the sol-gel techniques.

In the dentistry, monolithic net shaped implants have been used. Stanley et al. have been developed an Endosseous Ridge Maintenance Implant (ERMI) whose survival rate is higher than those do not contains bioactive glass [Stanley H.R. *et al.* 1997]. Osseointegration takes place at a rapid rate around the glass particles. This helps in stabilizing the boundary between the tooth and the periodontal membrane and the tooth is saved [Fetner A.E. *et al.* 1994]. Kokubo et al. have developed a glass ceramic system known as A/W glass based on $CaO-P_2O_5-SiO_2$ [Kokubo T. *et al.* 1986]. It contains the crystallites of apatite, β-wollastonite and some residual $CaO-SiO_2$ glassy phase [Nakamura T. *et al.* 1985]. The presence of crystallites enhances the mechanical properties e.g., fracture toughness, strength as well as subcritical crack growth velocity. The mechanism of bioactivity of such glass ceramics is similar to the bioactive glass. The most significant use of the bioactive glasses is in the dental porcelains for PFM bonding [Kontonasaki E. *et al.* 2008]. The dental porcelains are biocompatible but not bioactive and therefore incapable of interacting with the surrounding tissues. However, bioactive glasses and glass-ceramics are

bioactive and interact with body fluid forms the calcium phosphate rich surfaces allows them to bond tightly to hard and soft tissues [Chatzistavrou X. et al. 2010]. The addition of these materials into the dental porcelains will improve their bioactivity behavior.

1.19 Low-temperature glass frit (LTF)

The fusing temperature of crystalline silica is too high for use in veneering aesthetic layers bonded to metal substrates. At this temperature, alloys would melt and sag and CTE of crystalline silica is too low for these alloys. The tetrahedral network of silica can be break by the addition of alkali metal ions such as sodium, potassium, and calcium. These ions are associated with the oxygen atoms at the corners of the tetrahedra. As a result, the three-dimensional silica networks contain many linear chains of silica tetrahedra that can move easily at lower temperatures than the atoms, locked into the three-dimensional structure of silica tetrahedral, known as LTF. This ease of movement increases the fluidity (decreased viscosity) and CTE and reduces the softening temperature. An optimized amount of LTF should be added to the dental porcelains to maintain the balance between the fusing temperature and chemical durability. An extensive content of LTF may reduce the chemical durability and glass may crystalline during porcelain firing.

1.20 Bioactive glass-ceramic composites for dental applications

Nowadays, ceramic materials are used in the restorative dentistry because of specific properties such as durability in the oral environment, a similarity with natural tooth structure, high wear resistance and mechanical strength [Hussam M. *et al.* 2014, Milly H. *et al.* 2014]. Metal ceramic restorations (MCR) are commonly used due to their good fracture resistance [Denry I.L. 2001]. These consist of the metal substrate and several ceramic layers [Mrazova M. and Klouzkova A. 2009]. Feldspathic porcelains constituted by a

glassy aluminosilicate and crystalline leucite is mostly used for MCR [Mackert J.R. (b) *et al.* 1986].

The problem associated with the patient is the failure of fixed prosthetic due to cement dissolution and accumulation of the secondary carries [Felton D. A. *et al.* 1991, Kokoti M. *et al.* 2001, Walton J.N. *et al.* 1986]. Further, it results in a marginal gap between the fixed tooth and restoration causes a bacterial attack, the dissolution of the luting cement and pulp irritation and removal of the prosthesis [Ghaffari M. 2013, Waerhaug J. 1953].

For the last few years, research has been carried out for the development of bioactive dental materials for a complete and efficient attachment between the fixed prosthetic restorations and soft periodontal tissue [Ravarian R. *et al.* 2010]. These problems can be resolve by complete sealing of the marginal gap between the restoration and fixed tooth [Chatzistavrou X. *et al.* 2012]. It can be achieved by developing a hydroxyapatite surface layer to enrich tissue attachment, has been suggested as a novel approach. Dental ceramic materials are bio-inert and unable to interact with the surrounding tissues. According to L. L. Hench, a bioactive glass prompts a specific biological response at the interface of the hard tissue and the material [Hench L.L. and Paschall H.A. 1973, Goudouri O.M. *et al.* 2009]. Hydroxyapatite (HAp) layer is formed which enhances the cell proliferation and the cell attachment, thereby sealing the marginal gap [Craig R.G. and LeGeros R.Z. 1999, Meijering A.C. *et al.* 1998, Pitaru S. *et al.* 1988]. A series of surface reactions take place when the bioactive glass is exposed to an aqueous environment. These steps involve the exchange of alkali ions between the glass and water followed by a break down of the silica network and forms silanol bonds that polymerizes to form a hydrated, high surface area and

silica-rich layer. This leads to an enhancement in the migration of Ca^{2+} and PO_4^{3-} groups to the surface to form an amorphous CaP layer which further crystallized in an HCAp layer.

Over the last few years, research has been carried on the development of bioactive behavior of dental ceramics by adding the bioactive glass. Papadopoulou et al. have been reported the growth of a well-attached carbonate apatite layer on the surface of a bioactive glass coated on a dental ceramic substrate in SBF solution [Papadopoulou L. *et al.* 2003]. Kontonasaki et al. have investigated the surface structural change on the dental ceramics for MCR modified with a bioactive glass after immersion in SBF solution for several time periods [Kontonasaki E. *et al.* 2003]. They observed the development of a bioactive surface with active Ca-P nucleation sites. Chatzistavrou et al. have reported the growth of a hydroxyapatite layer on the surface of a bioactive glass coated the dental ceramic substrate [Chatzistavrou X. *et al.* 2010]. They suggested the feasibility of the developed material to be applied as a coating on the surface of dental porcelain. Microhardness test has also confirmed a good attachment of the coating and the strong bonding at the interface.

Kontonasaki et al. have constructed the six groups of modified ceramic specimens and studied their ability to support human periodontal ligament fibroblasts attachment and proliferation as compared to the dental porcelain [Kontonasaki E. *et al.* 2007]. The dental porcelain initially coated with the bioactive glass (PCB) or with a mixture of porcelain and bioactive glass (PCBP), the hydroxy-carbonate apatite (HCAp) layers have been bio-mimetically developed on both the surfaces (PCB and PCBP) after immersion in SBF [Kontonasaki E. *et al.* 2007]. They suggested that all the modified specimens supported the cell attachment, spreading and proliferation at a higher rate than the dental porcelain. Kontonasaki et al. have been developed the bioactive glass containing dental restorative

composites with sufficient mechanical properties comparable to the commercially available dental composites and also confirms the stability of these materials when exposed to a biologically challenging environment [Kontonasaki E. *et al.* 2008].

Recently, Chatzistavrou et al. have studied the sol-gel derived bioactive glass-ceramic composite material for the dental application [Chatzistavrou X. *et al.* 2012]. They found that the prepared bioactive glass ceramic composite shows the similar characteristics to that of a commercial dental ceramic [Chatzistavrou X. *et al.* 2012]. They also observed the cell attachment and proliferation of periodontal ligament and gingival fibroblasts cells on the surface of the developed material. They confirmed the bioactive behavior of the new materials and their ability to be potentially applied in dental restorations for soft tissue regeneration and sealing of the marginal gap.

Goudouri et al. have derived the bioactive glass ceramic composite with various ratios of the leucite based fluoroapatite glass ceramic using sol-gel route [Goudouri O.M. *et al.* 2011]. They observed that the prepared bioactive glass and dental composites surfaces were fully covered with the apatite layer after 18 days immersion in SBF with less mechanical integrity. Goudouri et al. have been further prepared the bioactive glass ceramic composite by combining the feldspathic dental ceramic and sol-gel derived bioactive glass in low percentage. They found that the prepared materials have an adequate mechanical property and low porosity, to withstand the occlusal forces during mastication [Goudouri O.M. *et al.* 2014]. In-vitro bioactivity of the sintered specimens has also been suggested after 21 days of immersion.

However, there is limited literature concerning the physicochemical properties of the wide range of dental ceramics used in the clinical practice. The microstructural analysis also

necessary because it provides an association between the composition, physical properties, and structural characteristics of the materials. Even fewer studies have focused on the biocompatibility or cytotoxicity of these prepared dental ceramics although they perform in direct contact with surrounding periodontal tissues. Furthermore, no work has been reported on the synthesis of mechanochemically derived leucite and kalsilite based bioactive glass-ceramic composites.

Furthermore, the addition of fine alumina to bioactive glass ceramic composite may increase the mechanical properties. Alumina has the biocompatibility, high hardness and excellent mechanical properties [Guazzato M. *et al.* 2004, Anusavice K.J. 2003]. The glass is toughened and strengthened when a crystalline material such as alumina is added to it. This is because the crack cannot pass through the fine alumina particles as easily as it can pass through the glass matrix. This technique has found the application in dentistry in the development of aluminous porcelain particles in a glassy porcelain matrix for porcelain jacket crowns [McCabe F. J. 2008]. Most dental ceramics that have a glassy matrix utilize reinforcement of the glass by a dispersed crystalline substance.