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Insights on Ceramics as Dental Materials. Part I: Ceramic Material Types in Dentistry

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Abstract Ceramics are widely used biomaterials in prosthetic dentistry due to their attractive clinical properties. They are aesthetically pleasing with their color, shade and luster, and they are chemically stable. The main constituents of dental ceramic are Si-based inorganic materials, such as feldspar, quartz, and silica. Traditional feldspar-based ceramics are also referred to as "Porcelain". The crucial difference between a regular ceramic and a dental ceramic is the proportion of feldspar, quartz, and silica contained in the ceramic. A dental ceramic is a multiphase system, *i.e.* it contains a dispersed crystalline phase surrounded by a continuous amorphous phase (a glassy phase). Modern dental ceramics contain a higher proportion of the crystalline phase that significantly improves the biomechanical properties of ceramics. Examples of these high crystalline ceramics include lithium disilicate and zirconia.

Keywords Dental ceramics · Silicates · Silica · Porcelain · Fracture toughness · Ceramic materials · Zirconia

1 Introduction to Si-based Inorganic Materials

Ceramics are formally defined as compounds of metallic and non-metallic elements consisting of oxides, nitrides, carbides, and silicates. Typical silicates are formed of Si-tetrahedrons, SiO_4^{4-}. The structure of ceramics exists in the form of crystalline solid or glasses [1]. Ceramics used in dentistry predominantly contain non-metallic and metallic elements [2] and are mostly based on silicon that is usually found in the form of silica (silicon dioxide), SiO_2, due to silicon's high affinity for oxygen. A vast array of Si-O compounds and silicate minerals exists in the Earth's crust [3, 4]. When silica occurs as a crystalline material, it can be in the form of quartz, crystobalite, and tridymite. Silica in dental ceramics is usually in the form of quartz [1]. Because of the black appearance of nitrides and carbides, they are not used as biomaterials in dentistry [2].

The traditional type of dental ceramics are feldspar-based materials containing silica fired at temperatures above 870°C and composed of a tectosilicate mineral feldspar ($KAlSi_3O_8$), quartz (SiO_2), and kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2 H_2O$) [5, 6]. Because feldspar-based ceramics were prone to failure owing to their inherent brittle nature, ceramics with higher crystalline content such as alumina (aluminum trioxide), Al_2O_3, and zirconia (zirconium dioxide) ZrO_2, were developed in order to improve the mechanical properties. High crystalline content ceramics are commonly used as the core (substructure) while feldspar-based ceramics are used as veneers to shield the core in prosthetic dentistry [7]. Interestingly, some calcium phosphate materials used for coating metallic subgingival dental implants are also considered ceramics, but will not be discussed in this paper [2]. Ceramics are very popular in dentistry because of their high biocompatibility and aesthetics [1].

2 Clinical Applications

Ceramics have three major indications in dentistry: a) ceramic-metal crowns and fixed partial dentures, b) all-ceramic restoration that consists of crowns, inlays, onlays, and veneers, short span anterior bridges, and c) ceramic

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denture teeth [1, 8]. A ceramic laminate veneer is used to cover an unsightly area by bonding to the facial surface of the prepared tooth [9]. In other areas of dentistry, certain ceramics are also used for the replacement of hard tissue [10]. Any contraindications have not been reported.

2.1 A Brief History of Dental Ceramics

It was in 1774 that the first porcelain denture was created by Alexis Duchateau in France. However, it was not until 1838 when Elias Wildman produced dental porcelain that had reasonably good translucency and shades to match natural teeth [1]. The first porcelain jacket crowns containing either feldspar or alumina (also known as aluminous) were created in the early 1900s. Even so, the poor match in the coefficients of thermal expansion between the framework base metal alloys and the veneer ceramics led to the development of leucite-containing feldspar ceramics in the 1960s. By adjusting the amounts of leucite, $K_2O \cdot Al_2O_3 \cdot 4SiO_2$, with feldspar glass, manufacturers had more control over the coefficient of thermal expansion of feldspathic porcelains and allowed the production of reliable ceramic-to-metal frameworks [11].

The last few decades have been intensively focused on developing restorations without a metal substructure known as all-ceramic restorations. Today, high strength core ceramics, such as zirconia, are more and more used as a substitute for the metal substructures in prosthetic dentistry [2, 12].

3 Structure of Dental Ceramics

Dental ceramics are multiphasic as they contain a dispersed crystalline phase surrounded by a translucent glassy phase. The glassy phase has the usual properties of glass such as brittleness, non-directional fracture pattern, and translucency while the crystalline phase contributes to the overall strength of the ceramic. Some newer dental ceramics differ from traditional dental ceramics in that a larger amount of crystals have been included. The addition of crystal content improves light scatter and opacity and aids in color adaption of transparent glassy phase to dental hard tissues (enamel and dentin). More crystals in the crystalline phase make the material more stable during firing and more resistant to stresses in the mouth. The overall gain of more crystals in the crystalline phase improves mechanical strength [1, 7].

3.1 Fusing Temperatures

Dental ceramics can be categorized by firing temperatures. Temperature ranges of 1315°C to 1370°C are attributed to 'High-Fusing Ceramics', temperature ranges of 1090°C–1260°C are called 'Medium-Fusing Ceramics,' and temperature ranges of 870°C–1065°C refer to 'Low-Fusing Ceramics.' High-fusing ceramics are used for denture teeth, medium-fusing ceramics for porcelain jacket restorations, and low-fusing ceramics for metal-ceramic restorations. Actually, a fourth category has been suggested described as ultra low-fusing ceramics. These ceramics are fired between 650°C and 850°C. High-fusing ceramics are superior in strength, insolubility, translucency, and accuracy during repeated firings compared to medium- and low-fusing ceramics [5, 11].

3.2 Type of Restoration

Ceramics can also be classified by restoration type as shown in Fig. 1. The two major categories are named a) All-Ceramic Restorations and b) Porcelain-Fused-to-Metals/Ceramic Metal Systems [5, 12].

All-ceramic materials in dentistry are composed of a wide range of crystalline phases and may contain up to 99% by volume of crystalline phase. The amount and particle size distribution of the crystalline phase determine the aesthetical appearance and biomechanical properties. All-ceramic materials can be fabricated by sintering, heat-pressing, slip-casting, and machining. A disadvantage of all-ceramic restorations is more tooth structure is removed to maximize the thickness of the restoration in order to reduce the risk of fracture. This may increase pulpal pathology in some individuals [2, 11–13].

The most traditional type of ceramic is feldspar-based that contains silica glasses. Feldspar-based ceramics are also known as 'Silica-Based Ceramics' and 'Feldspathic-Based Ceramics'. 'Porcelain' is a term often used to describe this type of ceramic because it contains high amounts of silica [12]. To be considered a feldspar-based ceramic, it should contain a minimum 15 wt% of silica or silicate [14]. Feldspar-based ceramics offer extremely pleasing aesthetics because they can mimic the colors and shades of natural tooth [12, 15], which make them good for veneers and inlays/onlays [8, 9]. Notable properties of feldspar-based ceramics are low density, resistant to chemical attacks, do not deteriorate with time, and very biocompatible [5–7, 11, 12, 16].

4 Composition of Feldspar-Based Ceramics

Feldspar-based ceramics are composed of $KAlSi_3O_8$, SiO_2, and kaolin, $Al_2O \cdot 2 SiO_2 \cdot 2 H_2O$. Kaolin is a hydrated aluminum silicate and its role is to bind the loosely held ceramic particles together. The amount of kaolin that can be used must be limited because kaolin is opaque and natural tooth is translucent. During the process of firing porcelain,
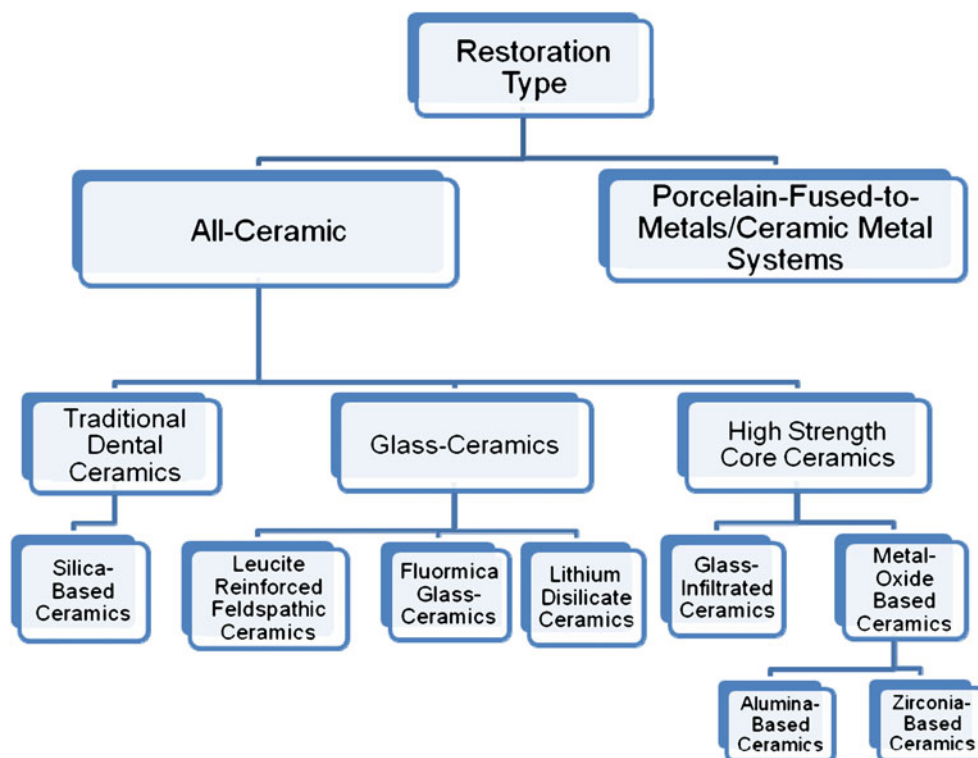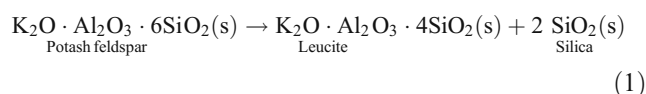
kaolin coats the non-fusible particles. Normally, less than 4% kaolin is contained in dental porcelain. After firing the ceramic, it is organized into a silica-based glassy matrix embedded in a core of crystalline substance containing silica and silicates, SiO_4^{4-}. Finally, they are milled to a fine powder. Silica is a reinforcing matrix component and the structure remains unchanged during the firing process. Quartz is not a strong material, so Al_2O_3 may be added as a reinforcing component. The proportion of quartz in porcelain is roughly 15% and contributes to the crystalline phase and translucency. Quartz also limits the shrinkage in porcelain [1, 5, 6].

Feldspar is a grayish crystalline mineral found in rocks of certain geographical locations. These rocks contain Fe and mica, nevertheless, iron is an impurity that needs to be removed mechanically by splitting the feldspar rocks and examining the thin splinters visually for the presence of the impurity. The pieces of feldspar need to be ground and milled to obtain the purest powder form of feldspar. Any remaining iron impurities are removed with strong magnets [5]. Upon firing, feldspar fuses together in the glassy matrix. Potash feldspar is a mixture of potassium aluminum silicate, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, which lowers the fusion temperature and viscosity and sodium aluminum silicate, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$, which increases the viscosity of molten glass [6].

To further improve traditional feldspar-based ceramics, leucite, $K_2O \cdot Al_2O_3 \cdot 4SiO_2$, crystals are added to the crystalline phase to enhance mechanical strength. Leucite crystals are created by further firing feldspar at 1150°C. A crystalline phase is formed and potash becomes leucite with the release of SiO_2 [6].

$$\underset{\text{Potash feldspar}}{K_2O \cdot Al_2O_3 \cdot 6SiO_2(s)} \rightarrow \underset{\text{Leucite}}{K_2O \cdot Al_2O_3 \cdot 4SiO_2(s)} + \underset{\text{Silica}}{2\ SiO_2(s)}$$
(1)

Leucite provides high translucency, strength, fluorescency, and opalescency and also determines the coefficient of expansion [1].

4.1 Properties of Silica-Based Ceramics

The compressive strength of porcelain is in the range of 350–550 MPa. However, its tensile strength is very low, only 20–60 MPa, because of the brittle glassy nature of porcelain. Feldspar-based ceramics lack fracture toughness and are very sensitive to surface microcracks. Thus, this type of ceramic is only suitable for low stress-bearing anterior applications because of a low wear resistance [1, 5, 6]. The shear strength of porcelain is reported to be around 110 MPa while the diametral tensile strength is about 34 MPa. Its flexural strength is found to be around 50–75 MPa, elastic modulus approximately 69–70 GPa, and an average surface hardness is about 460 KHN (Knoop's Hardness Number) compared to 340 KHN for enamel [5, 11]. Feldspar-based ceramics have little tolerance to plastic deformation and the coefficient of thermal expansion is about 13×10^{-6}/°C, which is surprisingly closely matching enamel and dentin [1, 13].

5 Glass-Ceramics

The so-called glass-ceramics are different from traditional feldspar-based ceramics because of the larger crystalline phase that helps stop crack growth. The presence of these crystals improves mechanical properties by reducing crack formation. The glassy phase fills the grain boundary to help create a pore-free structure. The crystalline phase grows during ceraming, *i.e.* conversion from a glass to a partially crystalline glass, and may occupy 50–100% of material [1, 5, 7]. The advantages of glass ceramics include great durability and the ability to bond to the tooth through the use of a resin luting composite [10, 13]. The properties of glass-ceramics depend on the crystal size, the density of crystals, and the interaction between the crystals and the matrix. Glass-ceramics are easier to fabricate than traditional ceramics and do not shrink much after firing. They are also highly translucent because the glassy matrix and the crystalline phase reduce internal light scattering [5].

The first developed and identified glass ceramic was a micaceous glass composed of 45 vol% glass and 55 vol% crystalline tetrasilicic fluormica, $SiO_2 \cdot K_2O \cdot MgO \cdot Al_2O_3 ZrO_2$, and further improvements elevated fluormica crystalline content to 70 vol%. Fluormica glass ceramics had flexure strength in the range of 120–150 MPa, which is suitable for anterior restorations but fluormica glass ceramics were eventually discontinued because of low tensile strength and poor survival rate in high stress areas in comparison to porcelain-fused-to-metal restorations [1, 17, 18].

Modern glass ceramics used today include leucite-reinforced and lithium disilicate ceramics. Developed in the 1990s, leucite-reinforced ceramics contain 45 vol% tetragonal leucite that dramatically improves the flexural strength to 120 MPa compared to feldspar-based ceramics. The fracture toughness of this type of ceramic is 1.6–1.8 MPa $m^{1/2}$, which is higher than traditional feldspar dental ceramics. It is noteworthy that this type of ceramic is used for veneers, and for anterior or posterior teeth [11, 14, 19]. Excellent aesthetics is attributed to the high translucency of leucite-reinforced ceramics [13].

Lithium disilicate, Li_2SiO_5, glasses have their flexure strength in the range of 350–450 MPa, which is even higher than that of leucite-reinforced ceramics. On the other hand, lithium disilicate glasses have a fracture toughness of 2.8–3.5 MPa $m^{1/2}$ [1, 20]. These desirable biomechanical properties make them suitable for short-span fixed partial dentures, posterior crowns, and all-ceramic bridges [13]. They are less aesthetic compared to other feldspar-based glasses, thus, lithium disilicate glasses are mainly used to construct the ceramic core that provides the strength while feldspar-based ceramics are used as veneers for aesthetic reasons. Within the core, 70 vol% consists of the primary crystalline phase containing lithium disilicates. Lithium disilicates contain many small, randomly-oriented, interlocking, plate-like crystals that deflect cracks. A second crystalline phase is also present consisting of lithium *ortho*phosphate, Li_3PO_4 [1]. Aesthetics of lithium disilicates can further be improved by veneering with an apatite-containing glass-ceramic [13].

There are differences in fracture toughness between leucite-reinforced and lithium disilicate-based ceramics because leucite-reinforced ceramics have small volume of crystals compared to lithium disilicate ceramics. Increasing crystallinity of lithium disilicate ceramics provides a tighter interlocking matrix, an increased strength, and a higher fracture toughness. Lithium disilicate ceramics may tolerate significantly higher fracture loads (705.5 N) than leucite-reinforced ceramics (470.3 N) when bonded to a resin composite [21].

6 High Strength Core Ceramics

Traditional feldspar-based ceramics used as jacket crowns were repeatedly prone to failure in stress-bearing conditions. The mechanisms of failure were related to micro-crack formation in the internal surface of the crown due to the firing and the cooling process. The hostile oral environment with its temperature shocks, pH fluctuation, masticatory forces, parafunctions *etc.,* promotes the stressful conditions and the inner porcelain surface is subjected to tensile stresses, allowing micro-cracks to propagate. Eventually, the cracks would reach the outer surface and it was time for a new jacket crown replacement [5].

Several ways were developed to strengthen dental ceramics: one example of them was to reinforce the core of the ceramic. The other is to combine feldspar-based ceramics with a metallic substructure [21]. Core ceramics consist of an aesthetic ceramic supported by another ceramic that provides the core and strength but lacks the desired aesthetics. Such contemporary oxide ceramics are pure alumina and zirconia in the crystalline matrix [13, 22]. As such they are single phase microstructure without a glassy phase. Pure alumina cores contain 99.5% alumina and have their flexure strength around 487–699 MPa and fracture toughness about 4.48–6 MPa $m^{1/2}$ [20, 23, 24]. On the other hand, pure zirconia has a flexure strength of 1000 MPa and its fracture toughness is around 10.00 MPa $m^{1/2}$. Feldspar-based veneers are applied to them because zirconia and alumina as substructures are opaque and dull in color. Zirconia is usually manufactured as pre-sintered blocks that may shrink up to 20% upon firing [7]. With attractive mechanical properties, however, there comes a drawback, *viz.* high crystalline ceramics cannot be acid etched for bonding with resin composite luting cements [13].

6.1 Glass-Infiltrated Ceramics

Glass-infiltrated ceramics contain a porous core which consists of 85% alumina infiltrated with lanthanum oxide, La_2O_3, glass. The interpenetrating phases of the two types of materials improve fracture resistance and may stop crack growth. The fracture toughness is reported to range from 2.48 to 3.55 MPa $m^{1/2}$ and flexure strength is around 300–500 MPa [7]. Cracks cannot propagate through alumina particles as easily as glass [13]. Applications of glass-infiltrated ceramics include substructures for anterior or posterior single crown and short span anterior partial dentures [1]. Table 1 lists the commercial availability of these types of ceramics.

6.2 Porcelain-Fused-to-Metal Restorations

All-ceramic restorations may be described as very pleasant looking. However, they are in principle brittle and may fracture in the stressful oral environment. On the other hand, all-metal/alloy restorations are strong, yet they lack aesthetics. By combining both materials together, a composite structure can be made consisting of the strength and toughness of metal with the aesthetics of porcelain, known as porcelain-fused-to-metals, PFM, or ceramics-metal systems [6, 12, 19]. PFM is prepared with a cast metal alloy, such as Co-Cr and Au-Pd, and porcelain which is then fused onto the metal surface shielding the unpleasant appearance of metal or alloy. However, only an opaque shade, such as TiO_2, may be applied to mask the metal appearance of metal substructure. The opaque shade makes the restoration unnatural compared to all ceramic restorations and metal alloys may elicit allergic reactions [5].

7 Processes of Fabrication

There are many techniques to fabricate all-ceramic restorations such as layering/sintering, heat pressing, slip casting

Table 1 Some main dental ceramics manufacturers

Type of Ceramic	Available (Manufacturer)
Leucite-reinforced	IPS Empress (Ivoclar Vivadent, Schaan, Liechtenstein)
Lithium Disilicate	IPS e.max (Ivoclar Vivadent, Schaan, Liechtenstein)
Pure alumina	Procera AllCeram (Nobel Biocare, Stockholm, Sweden)
Pure zirconia	Lava (3M/ESPE, Neuss, Germany)
Glass-infiltrated	In Ceram Alumina (Vita Zahnfabrik, Bad Säckingen, Germany)
Leucite feldspar-based	Vitablocs Mark II (Vita Zahnfabrik, Bad Säckingen, Germany)

and glass-infiltration, and machining. PFM restoration fabrications require refining the surface of the metal and bringing out the desired oxide layer prior to firing the ceramic onto the metal.

7.1 Layering and Sintering

First, a slurry is prepared by mixing ceramic powder with modeling fluid or distilled water and the slurry is then applied in layers to a refractory die. The applied ceramic mass is blotted in order to make the piece as dense and pore free as possible before sintering. The layered piece is placed in the ceramic furnace and sintered at the required temperature, which is usually 900°C. The sintering must be performed in vacuum so that air can escape during heating from the mass. The final product will shrink 40%, therefore, the modeled piece must be larger in size. Layering is commonly used to fabricate veneers but there is always a risk of delamination because it is inevitable that some pores will be present [1, 7]. A majority of all-ceramic restorations are sintered [12].

7.2 Heat Pressing and Hot Pressing

Heat pressed ceramics are fabricated using the lost wax technique performed by modeling the restoration in wax and then investing the restoration in a refractory die that forms the substructure. A highly external pressure presses the pre-sintered ingot blocks such as leucite-reinforced or lithium disilicate glass ceramics into a mold created by the burned out wax. The blocks are sintered and shaped at temperatures as high as 1180°C to produce all-ceramic crowns, inlays, onlays, veneers, and fixed partial dentures [1, 10, 11].

7.3 Slip Casting and Glass-Infiltration Fabrication

Fine-grained Al_2O_3 powder is mixed with de-ionized water to produce a slip that is applied in layers to a gypsum die to build the substructure. Water is removed from the porous gypsum by capillary action in order for the particles to be packed closer and as dense as possible. Core materials contain approximately 85% Al_2O_3 [5, 25]. The alumina core is then slowly fired up to 120°C to remove the water and the binding agent. The firing is gradually increased to 1120°C for 2 h with very minimal shrinkage, about 0.2%. The final structure is a porous and interconnected ceramic network between the inner and the outer surface. The porous alumina substructure is glass-infiltrated with lanthanum aluminosilicate, $LaAl_2O_3SiO_2$, glass. The substructure is placed on a platinum-gold alloy sheet and fired in a furnace to 1100°C for 4–6 h. The glass particles melt and infiltrate into the pores by capillary diffusion [5, 7]. The

final product contains lesser pores, lesser flaws, and higher toughness than traditional feldspar-based ceramics. Zirconia and spinel, $MgAl_2O_4$, can be substituted for alumina as the core. Spinel has better aesthetics than alumina, but a compromise is a lower flexure strength, 300 MPa, while zirconia has a higher flexure strength, 700 MPa, than alumina except a tradeoff to improve strength is less translucency [1].

7.4 Machining

Machine systems use industrially manufactured ceramic blocks to produce high quality ceramic restorations. A replica of the restoration made of resin composite is fabricated on a master cast and a scanning tool traces the replica. The restoration is produced by a copy milling machine using a ceramic block [7].

However, these copy milling systems are slowly being replaced by CAD/CAM (Computer-Assisted Design-Computer-Assisted-Manufacture) systems. CAD/CAM systems create an optical impression of the tooth replica and the computer designs the restoration. The replica is scanned by a laser with pictures being taken while the die is rotated and the CAD/CAM system replicates the restoration by diamond milling a replica using a densely sintered ceramic blank [13, 26]. Scanning technology has advanced to using short wavelength blue light capable of capturing a high precision image and with a reduction in scanning time [27].

7.5 Fabrication of PFM Restorations

First, the metal surface must be ground or sandblasted to remove unwanted oxides and other residues to increase surface roughness, hence, improving micromechanical interlocking between the metal and ceramic. Then, the metal must be heated under vacuum to create the desired oxide coating by allowing metallic elements, such as Sn and Zn to rise upon the surface and form the oxide surface layer. Then, the third step is to remove unwanted oxide layer by acid pickling using 50% or 30% hydrofluoric acid. Lastly, a further treatment on the metal surface is carried out to create the desired thickness and quality of the oxide layer [1, 12].

An opaque feldspar ceramic is then fired onto the metal to hide the metal substructure. The coefficient of expansion of the metal must be greater than the coefficient of expansion of the ceramic to keep the ceramic under a state of compression caused by the metal attempting to shrink. This reduces the chance of cracking within the ceramic since the ceramic must overcome the compressive stresses [12]. Alternatively, smaller diameter sodium ions can be replaced with larger diameter potassium ions on the feldspar ceramic to put the ceramic under compression in order to minimize crack formation between the ceramic and

the metal [28]. Reported improvements of 50% increased flexure strength and 100% improved fracture toughness are found with feldspar ceramics [29, 30].

8 Summary

We may claim that ceramics will continue to play an important role in dentistry owing to their natural aesthetics and biocompatibility. However, there will always be a compromise between aesthetics and the biomechanical strength. Good translucency requires a higher content of the glassy phase and good strength requires a higher content of the crystalline phase. Given this, there need to be a balance between the two material phases. As an idea, other types of crystals should be sought that inhibit crack growth. However, they should not contribute much by volume to the overall ceramics in order to reduce crystalline content and enhance translucency with a greater glass content. The most common clinical failures in all-ceramic and PFM restorations are delamination (chipping) and crack initiation. Bearing this in mind, careful attention must be paid to good adhesion between the restoration and the tooth tissues. The direction of dental ceramics is shifting away from using base and noble metal alloys because they may contain allergens (such as Be and Ni) and more research needs to be devoted to all-ceramic materials because of their high, promising biocompatibility.

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