CHAPTER 2
LITERATURE REVIEW

In this chapter, attention is divided to focus on the dental porcelains, all-ceramic restoration, leucite, zirconia and the ceramic nanocomposites. It is first necessary to describe the information background of dental porcelains. The relevant literatures on chemical composition, structure, and application of dental porcelains are reviewed. The second part is chemical composition and structure of leucite, and development of leucite reinforced dental porcelains. The third part is chemical composition, structure of zirconia, and zirconia reinforced dental porcelains. Finally, the concept of ceramic nanocomposites and its application in dental ceramics is described in more details.

2.1 Dental porcelains

2.1.1 Historical perspective

Ceramics are generally defined as "inorganic, non-metallic materials". Biomaterials are now defined as "natural or synthetic materials suitable for introduction into living tissue especially as part of a medical device". Considering these definitions, the ceramics have been used as biomaterials for humans. In 1972, indeed, Amadeo Bobbio discovered Mayan skulls, some of them more than 4000 years old, in which missing teeth had been replaced by nacre substitutes. Nacre is a natural composite consisting of 95–98 wt% of calcium carbonate (aragonite, the 'ceramic' phase) and 2–5 wt% of organic matter (fibrous proteins, polysaccharides) [10].

Modern dentistry is said to have its beginnings during the year 1728, when Fauchard published a treatise describing many types of dental restorations, including a method for the construction of artificial dentures from ivory. Since the first use of porcelain to make a complete denture by Alexis Duchateau in 1774, numerous dental porcelain compositions have been developed. The year 1792 is important as the date when de Chamant patented a process for the construction of porcelain teeth; this was followed early in the next century by the introduction of the porcelain inlay.

Following the introduction of the first feldspathic porcelain crown by Land in 1903 [11], the interest and demand for nonmetallic and biocompatible restorative materials increased for clinicians and patients.

However, since Taggart introduced the technique of cast metal restorations in 1907, metals have been accepted as the most reliable dental restorations because of higher mechanical strength and easier preparation than ceramics. Sixty years later, porcelain compositions suitable for metal-ceramic restorations were introduced in 1962 [12] and led to the success of this technology. The reinforcement of aluminous core and veneer porcelains was first achieved as a result of the work of McLean and Hughes in 1965 [13]. Further materials developments were based on increasing the crystalline content, for example leucite (Empress), mica (Dicor), hydroxyapatite (Cerapearl) or mixed glass oxides (In-Ceram) [14]. For the last ten years, the application of high-technology processes to dental ceramics allowed for the development of new materials such as heat pressed, injection-molded, slip-cast ceramics, glass ceramics, and computer-aided design and computer-aided manufacturing (CAD/CAM).

2.1.2 Chemical Compositions

The earliest dental porcelains were mixture of kaolin, feldspar and quartz, and were quite different for porcelain artware, sanitary ware, and china dinnerware as indicated in Fig. 2.1. It was not until 1838 that Elias Wildman produced dental porcelain with the translucency and shades that reasonably matched those of natural teeth. The compositions for domestic and dental porcelain are shown in Table 2.1. Indeed, the dental porcelains contain little of clay and, possible, would be more aptly described as dental glasses. Kaolin or clay ($Al_2O_3.2SiO_2.2H_2O$) is a hydrated aluminosilicate, the set decorative porcelain is essentially a mixture of this with silica, bound together by a flux or binder such as feldspar which is a mixture of potassium ($K_2O.Al_2O_3.6SiO_2$) and sodium aluminosilicates ($Na_2O.Al_2O_3.6SiO_2$) [15]. Kaolin is opaque; however, and when present, even in very small quantities, it meant that the earliest dental porcelain lacked adequate translucency. Quartz remains unchanged during the sintering process and acts as a strengthening agent. It is present as a fine

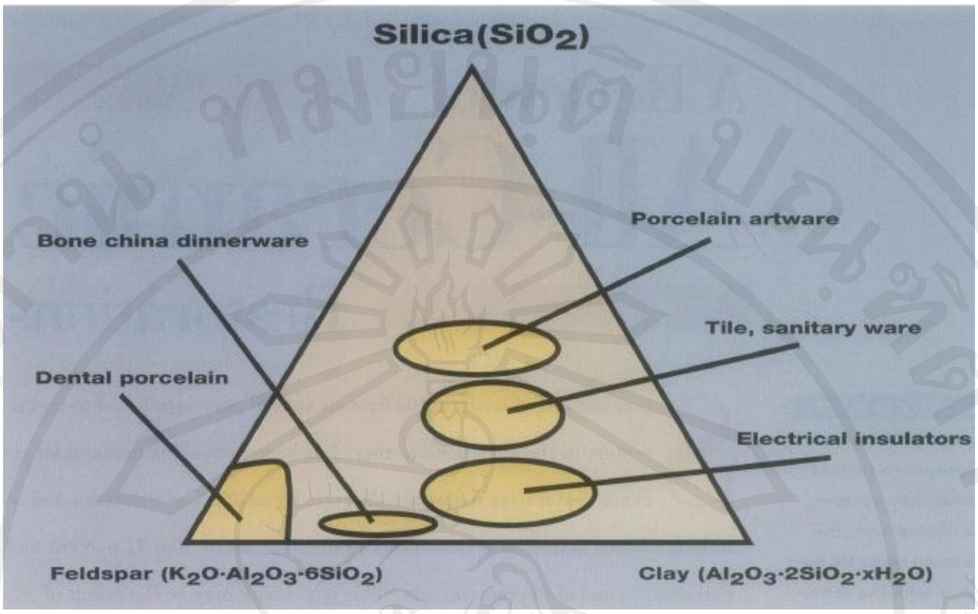

Fig. 2.1 White ware compositions composed of clay, feldspar, and silica (quarts) [16].

Table 2.1 Composition of household and dental porcelains [17].

Type of Porcelain	**Compositions (wt%)**			
	Kaolin	**Quartz**	**Feldspar**	**Glass**
Household	50	20–25	25–30	0
Dental	0	25	60	15

crystalline dispersion throughout the glassy phase that is produced by the melting of feldspar. Feldspar fuses when it melts, forming a glass matrix. Feldspars are mixtures of potassium aluminosilicate and sodium aluminosilicate, also known as albite. Feldspars are naturally occurring substances, so the ratio between potash (K_2O) and soda (Na_2O) will vary somewhat. This affects the properties of feldspar, in that soda tends to lower the fusion temperature and potash increases the viscosity of the molten glass. During the firing of porcelain there is always the danger of excessive pyroplastic flow, which may result in rounding of the edges and loss of tooth form [15]. It is important that the correct amount of potash is present to prevent this. These alkalis are present either as a part of feldspars, or they may be added as carbonates to ensure the correct ratio. Chemical composition analysis of several commercial dental porcelains is given in Table 2.2 [17].

Table 2.2 Chemical composition analysis of some commercial dental porcelains [17].

Compositions	**Commercial dental porcelains**			
	Ceramco opaque[a] **(wt%)**	**VMK opaque**[b] **(wt%)**	**Ceramco dentin**[a] **(wt%)**	**VMK dentin**[b] **(wt%)**
SiO_2	55.10	52.41	62.20	56.83
Al_2O_3	11.65	15.15	13.40	16.30
CaO	-	-	0.98	2.01
K_2O	9.60	9.90	11.30	10.25
Na_2O	4.75	6.58	5.37	8.63
TiO_2	-	2.59	-	0.27
ZrO_2	0.16	5.16	0.34	1.22
SnO_2	15.0	4.90	0.50	-
Rb_2O	0.04	0.08	0.06	0.10
ZnO	0.26	-	-	-
UO_3	-	-	-	0.67
B_2O_3, CO_2, H_2O	3.54	3.24	5.85	3.75

[a] Dentsply Ceramco R and D, USA; [b] VITA Zahnfabrik, Germany

2.1.3 Structures

Dental porcelains are, in part, glassy materials and in order to understand their formulation, knowledge of glass formation is essential. Glasses may be regarded as supercooled liquids or as non-crystalline solids. This lack of crystalline distinguishes them from other solids, and their atomic structures and properties depend, not only on composition, but also on thermal history. The glass-marker selects complex or impure solutions in order to modify the physical properties of the glass both in the molten and solid form. These properties would include viscosity, melting temperature, chemical durability, thermal expansion and resistance to devitrification. Frictional forces inhibiting the formation of new molecular configurations in the liquid glass should also be as high as possible. This can be achieved by rapid cooling or preferably, for dental purposes, by using materials that produce high viscosity in the melt, e.g. aluminium oxide (Al_2O_3) [18]. The principle anion present in all glasses is oxygen ion which forms very stable bonds with small multivalent cations such as silicon, boron, germanium, or phosphorous, giving rise to structural units, such as the SiO_4 tetrahedra illustrated in Fig. 2.2, which form a random network in glass [19, 20]. These ions are thus termed glass formers. Zachariasen [21] examined the characteristics of these glass forming oxides and proposed his random network theory of glass structure. He considered that the interatomic forces in glasses and crystals must be essentially similar and that the atoms in glass oscillate about definite equilibrium positions. He deduced that the atoms must be linked in the form of a three-dimensional network in glass as in crystals. Since glasses do not give a sharp X-ray diffraction spectrum, it could not be periodic (in an ordered arrangement). Zachariasen considered that although the units of structure in the glass, (i.e. SiO_4 tetrahedra) and in the crystals are practically identical, in the crystal these structural units are built up to give a regular lattice. By contrast, in the glass there is sufficient distortion of bond angles to permit the structural units to be arranged in a random network (Fig. 2.3). Zachariasen proposed certain conditions for glass formation:

(1) An oxygen atom must not be linked to more than to M atoms,

(2) The number of oxygen atoms surrounding M must be small

(3) These oxygen polyhadra must share corners only and not edges or faces.

(4) At least three corners of each polyhedron should be shared

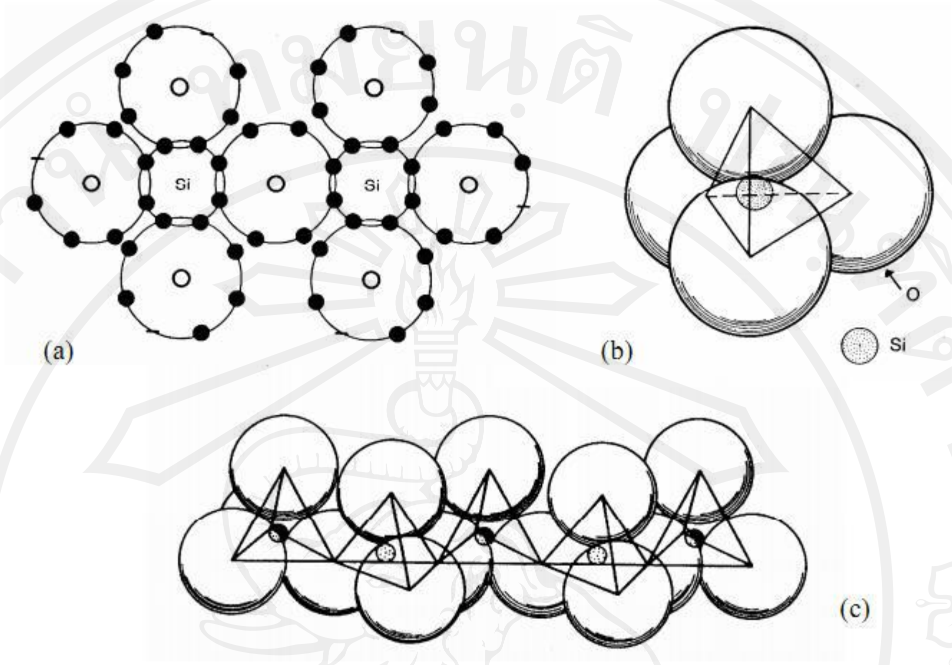

Fig. 2.2 Structural units of SiO_4 tetrahedra: (a) diagram of silicate unit with each SiO tetrahedra sharing an oxygen atom, (b) a silicate unit which the silicon atom (Si) is surrounded by four oxygen atoms (oxygen polyhedra) and (c) linked silicate units which form the network in glass [22].

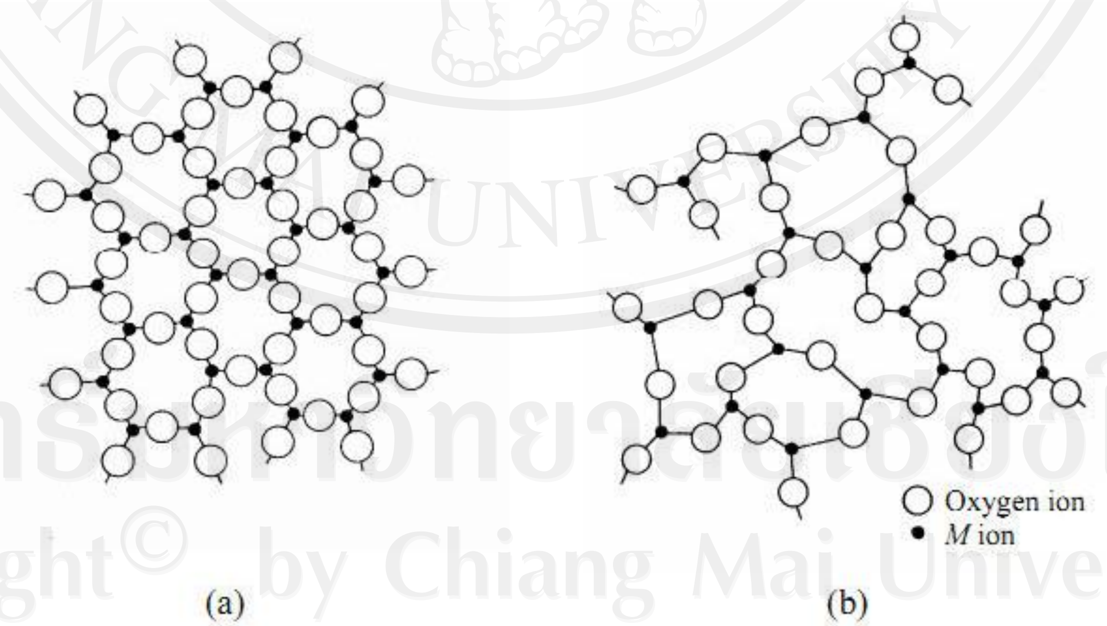

Fig. 2.3 Two-dimensional presentation of an oxide M_2O_3 in (a) the crystalline form and (b) the glass form [22].

For dental purposes [9], only two glass-forming oxides are used – silica and boron oxide - and they form the principal network around which a dental glass can be built. Alumina under certain circumstances may be regarded as a glass-forming oxide when in combination with other oxides. Dental porcelains use the basic silicon-oxygen network as the glass-forming matrix but additional properties, such as low fusing temperature, high viscosity, and resistance to devitrification, are built in by the addition of other oxides to the glass-forming lattice SiO_4. These oxides generally consist of potassium, sodium, calcium, aluminium and boric oxides. The purpose of a flux is principally to lower the softening temperature of a glass by reducing the amount of cross-linking between the oxygen and glass- forming elements, e.g. silicon. For example, if soda (Na_2O) is introduced into silicate melt to produce sodium silicate glasses, structural changes occur as in Fig. 2.4. Instead of the bridging oxygen ions which formed the link between the two SiO_4 tetrahedra, there are now two non-bridging oxygen, one of which has been contributed by the sodium oxide. A gap is therefore produced in the SiO_4 network and the sodium ions are accommodated in the interstices or holes in the random network structure as shown in Fig. 2.5. The greater the number of Na^+ ions added, the more Si-O-Si bridges are broken. The O:Si ratio in a glass is of the greatest importance and will affect both the viscosity of the glass and its thermal expansion. For example, in dental porcelain used for bonding the metal, it is usual practice to increase the soda content in order to raise the thermal expansion of the porcelain near to that of the gold alloys. Other alkali metal oxides, such as lithium or potassium oxides, take part in the glass structure in a similar manner [23, 24]. Lithium ions will be accommodated in smaller structural interstices and the sodium ions and the potassium ions in larger one. MgO, CaO and BaO may also act as modifying oxides [25, 26]. The used of these alkali metal oxides must be very carefully controlled to preserve the original glass-forming network; otherwise, problems of devitrification may occur. Potassium, sodium or calcium oxides are introduced into a glass melt via their respective carbonates which revert to oxides on heating.

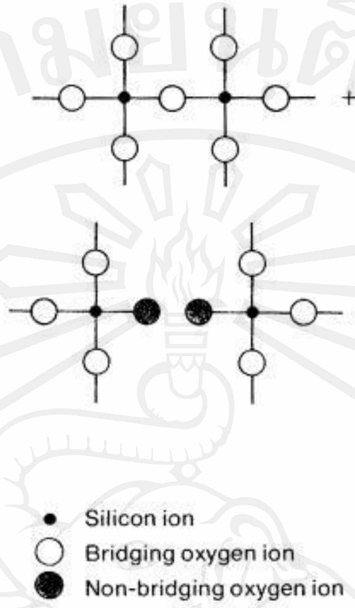

Fig. 2.4 Reaction between sodium oxide and silica tetrahedral [22]. The sodium oxide contributes one of the non-bridging oxygen ions which interrupt the continuity of the silica network. (For simplicity, only a two-dimensional representation of the SiO_4 groups is given; in the actual glass structure these groups take the form of tetrahedral as illustrated in Fig. 2.2)

The addition of glass modifiers or fluxes to the basic glass-forming network SiO_4 in dental porcelain will not only lower the softening point but also decreases the viscosity [27]. Dental porcelains require a high resistance to slump or pyroplastic flow and it is therefore necessary to produce glasses with a high viscosity as well as low firing temperatures. This can be done by using intermediate oxides which although not usually capable of forming a glass, can take part in the glass network.

The hardness and viscosity of a glass can be increased by the use of an intermediate oxide such as aluminium oxide (Al_2O_3) [28]. The role of Al_2O_3 in glass formation is complicated. It cannot be considered as a true glass former by itself because the dimensions of the ion exclude the possibility of Al_2O_3 triangles being formed and the O:Al ratio precludes the formation of AlO_4 tetrahedra. In crystals, the aluminium ion can be four or six coordinated with oxygen giving rise to tetrahedral

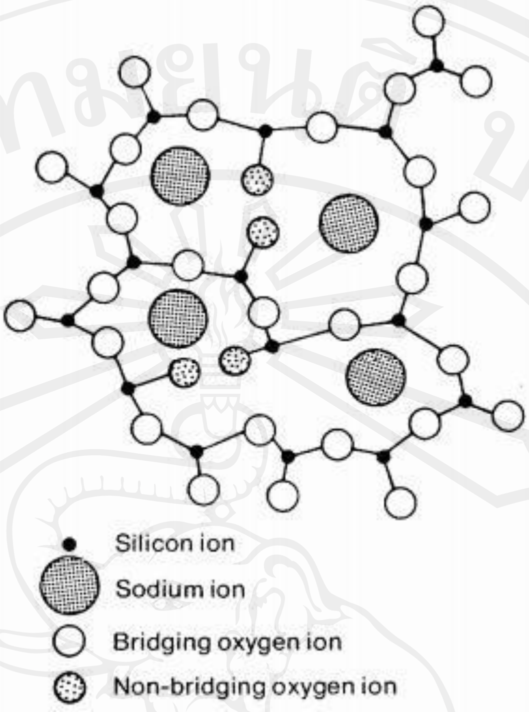

Fig. 2.5 Two-dimensional representation of the structure of sodium silicate glass [22]. (The structure is shown in a simplified form since only three of the four oxygen ions surrounding each silicon ion are depicted.)

AlO_4 or octahedral AlO_6 groups [29]. The tetrahedral groups can replace SiO_4 tetrahedra in silicate lattices to give the arrangement were shown in Fig. 2.6. Since each aluminium ion has a charge of +3 as compared with a charge of +4 for each silicon ion, an additional unit positive charge must be present to ensure electroneutrality. When metallic oxides, such as sodium oxide, are present, one alkali metal ion per AlO_4 tetrahedron would satisfy this requirement and the alkali metal ions could be accommodated in the interstices between tetrahedral groups. In this way, as each Al^{3+} ion replaces a Si^{4+} ion in the network, one Na^+ ion is taken into preserve neutrality. This type of structural arrangement is found for many alumino-silicates such as feldspars and zeolites, where the crystals are built up of linked SiO_4 and AlO_4 groups [30, 31].

Large univalent or divalent cations are present in these structures to the extent of one alkali ion or "half" an alkaline earth ion per AlO_4 tetrahedron. A similar situation probably exists in a glass network where the electroneutrality requirement imposes the condition that each gram-molecule of aluminium oxide present in the glass requires the presence also of one gram-molecule of an alkali oxide or alkali earthoxide. This rule is obeyed for many types of aluminosilicate glass [30, 31].

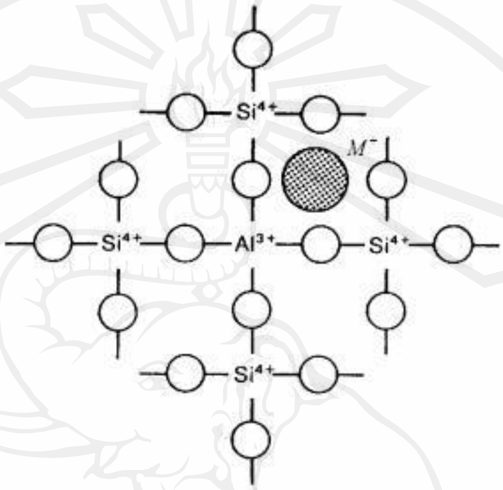

Fig. 2.6 Aluminium is in a silicate network (The structure is shown in a simplified form; the true structure is three-dimensional, the AlO_4 and SiO_4 groups having tetrahedral configurations.). The alkali metal ion (M^+) such a sodium maintains electroneutrality [22].

2.1.4 Application in dental field

The dental profession has always been in search of restorations that have a “natural” appearance but are, as the same time, long lasting. Traditionally, dental porcelains are used in construction of artificial teeth for dentures, crowns and bridges. From the 1980s onwards the use of porcelains has been extended to include veneers, inlays/onlays (Fig. 2.7a), crowns (Fig. 2.7b), and bridges (Fig. 2.7c). In spite of their excellent esthetic qualities and their good biological compatibility of dental porcelain; however, these porcelain based materials still lacked mechanical strength. Therefore, during the last 200 years, a global approach has been to increase the content of ceramic: from silica to alumina reinforced porcelain (in 1960), to glass-infiltrated high strength ceramics (alumina or zirconia) and finally to monolithic ceramics [32]. One of the most serious drawbacks with the early dental porcelains described above was their lack of strength and toughness, which seriously limited their use. In order to overcome the problem of lack of strength and toughness of dental porcelains, there are two possible solutions to solve the problem. One solution is to provide the dental porcelain with support from a stronger substructure, such porcelain-fused-to-metal (PFM) (Fig. 2.8a). The other option is to produce ceramics, which are stronger and tougher. Several methods are used to improve the strength and clinical performance of dental ceramics, including crystalline reinforcement, chemical strengthening, and thermal tempering [33].

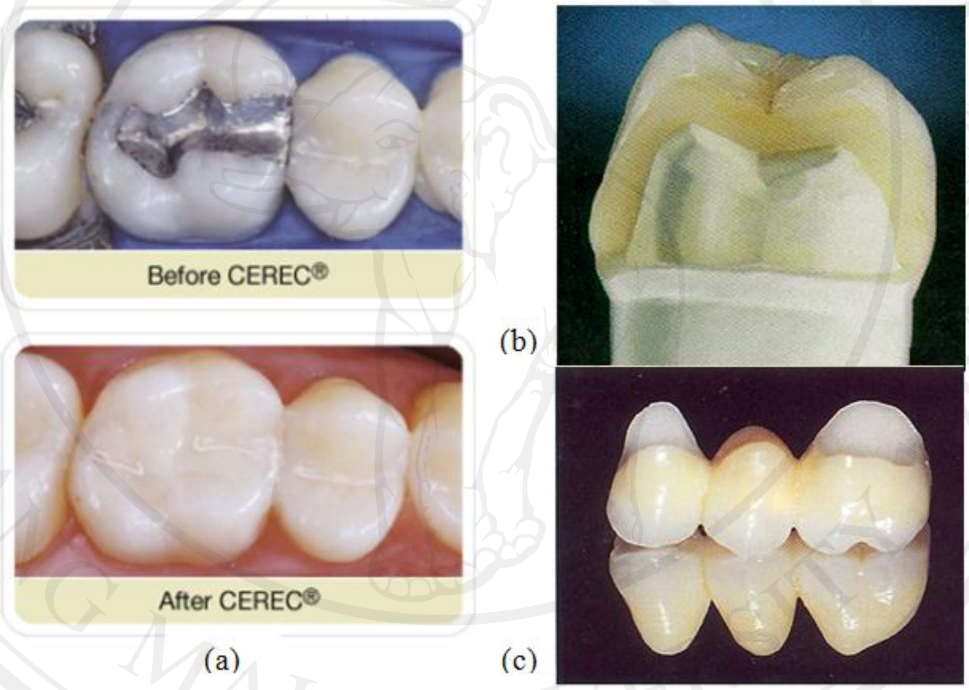

Fig. 2.7 Applications of dental porcelain-based ceramics: (a) inlay, (b) all-ceramic crown [34], and (c) bridge [35] .

Strengthening by crystalline reinforcement involves the introduction of a high proportion of the crystalline phase into the ceramic to improve its resistance to crack propagation (Fig. 2.8b). Dental ceramics have a composite structure. Materials for metal-ceramic restorations contain a vitreous phase, also called glassy matrix, that represents 75 to 85% by volume and are reinforced by various crystalline phases [36]. The dental porcelain could be strengthened by the dispersion of ceramic crystals of high strength and elastic modulus with glassy matrix. However, the crystalline phase

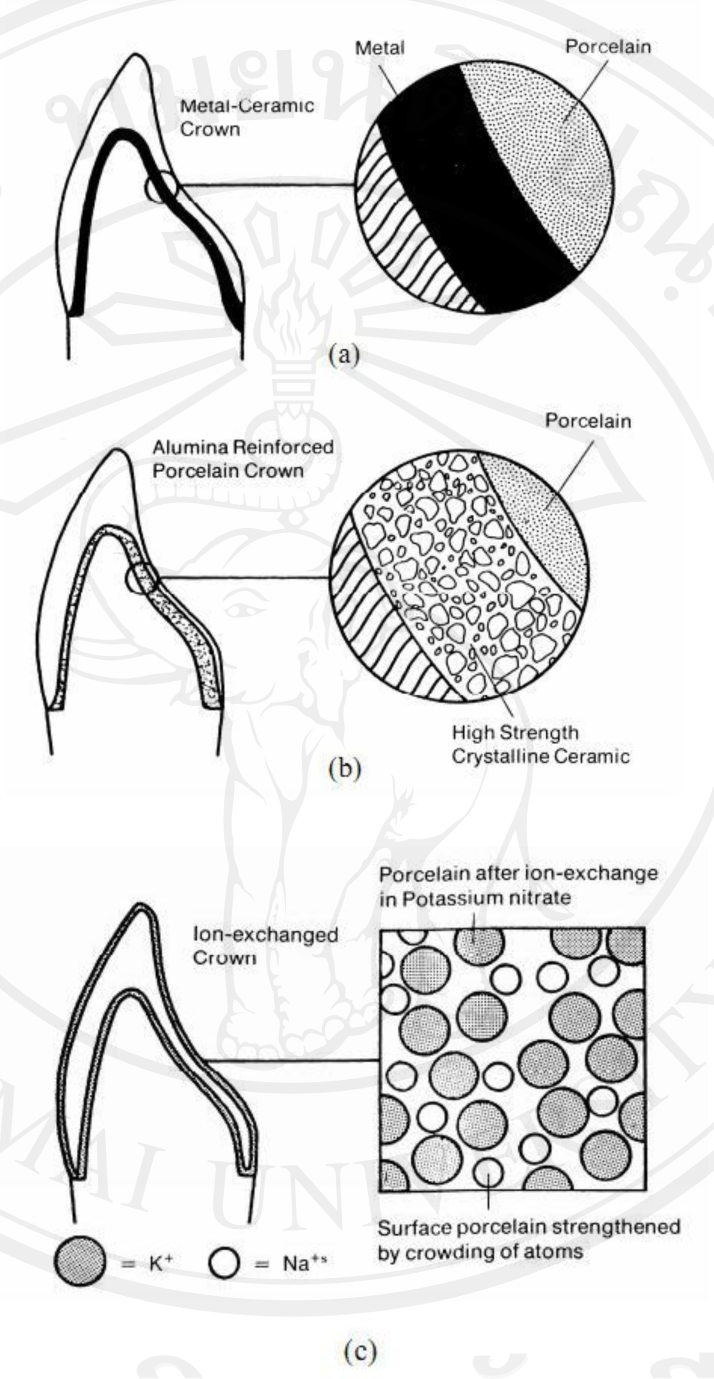

Fig. 2.8 Methods of strengthening dental porcelain: (a) metal substructure, (b) reinforcing of high strength crystalline ceramics, and (c) production of pre-stressed surface layers in dental porcelain via ion-exchange [33].

must be carefully selected. The choice of the crystalline phase in compositions for metal-ceramic restorations was initially dictated by the need for matching the thermal contraction coefficient of the porcelain close to that of the metallic infrastructure in order to avoid the development of tensile stresses within the porcelain when cooled. Therefore, important selection criteria include the coefficient of thermal contraction, toughness, and the modulus of elasticity. Mclean and Hughes [13] used this method to develop the first aluminous porcelains for the fabrication of crowns. These reinforced porcelain had strengths of up to 180 MPa-approximately double that of the more conventional feldspathic materials.

Chemical strengthening is another method used to increase the strength of glasses and ceramics. The principle of chemical strengthening relies on the exchange of small alkali ions for larger ions below the strain point of the ceramic (Fig. 2.8c). Since stress relaxation is not possible in this temperature range, the exchange leads to the creation of a compressive layer at the surface of the ceramic [37]. Finally, any applied load must first overcome this built-in compression layer before the surface can be placed into tension, resulting in an increase in fracture resistance. This technique involves the use of alkali salts with a melting point lower than the glass transition temperature of the ceramic materials. Ion-exchange strengthening has been reported to increase the flexural strength of feldspathic dental porcelain up to 80%, depending on the ionic species involved and the composition of the porcelain [38, 39]. The depth of the ion-exchanged layer has been shown to be greater than 50 micrometers [40]. However, this technique is diffusion-driven, and its kinetics is limited by factors such as time, temperature, and ionic radius of the exchanged ions.

Thermal tempering is commonly used to strengthen glasses and is based on the creation of temperature gradients between the surface and the bulk part of the glass piece. The technique involves heating of the glass to a temperature above the glass transition region and below the softening point. It is then cooled to room temperature in a jet of air or, in some cases, in an oil bath. The residual stresses arise from differences in cooling rates for surface and interior regions. The result is similar to that obtained with chemical strengthening with the formation of a surface compressive layer that results in increased strength. This technique has been successfully applied to feldspathic dental porcelain and resulted in mean flexure strength values 2.6 times greater than the corresponding value for slow-cooled specimens [41]. The stress relaxation behavior of dental porcelain when reheated can be characterized by stress relaxation testing under compression at high temperature [42] or by acoustic emission techniques [43]. The principal effect of tempering is the inhibition of crack formation rather than the retardation of crack growth [41]. However, the combination of thermal tempering and subsequent ion-exchange does not lead to a significant increase in the mean biaxial flexural strength values [44]. One last method commonly used to strengthen ceramics is the glazing procedure. The principle is the formation of a low-expansion surface layer formed at high temperature. When cooled, the low-expansion glaze places the surface of the ceramic in compression and reduces the depth and width of surface flaws. However, glazing does not significantly improve the biaxial flexure strength of feldspathic dental porcelain [24].

Porcelain-fused-to-metal (PFM) restorations are the most effective and widely used system in dental ceramics. They combine the strength of metal with esthetic quality of the ceramic materials. The big disadvantage of this restoration lies in the increased light reflectivity from the opaque porcelains that are used to mask the metal coping. A natural tooth diffuses and transmits light, whereas a PFM restoration violates this property. It will only diffuse and reflex the light in the body area. As a result, PFM restorations often look brighter in the mouth. The absence of the metal framework in all-ceramic restorations minimizes the undesirable light reflection produced by opaque layer. The veneer porcelains are more translucent compared to those formulated for PFM restorations. Therefore, increased light transmission and diffusion can be achieved, resulting in translucency with depth [45] (Fig. 2.9).

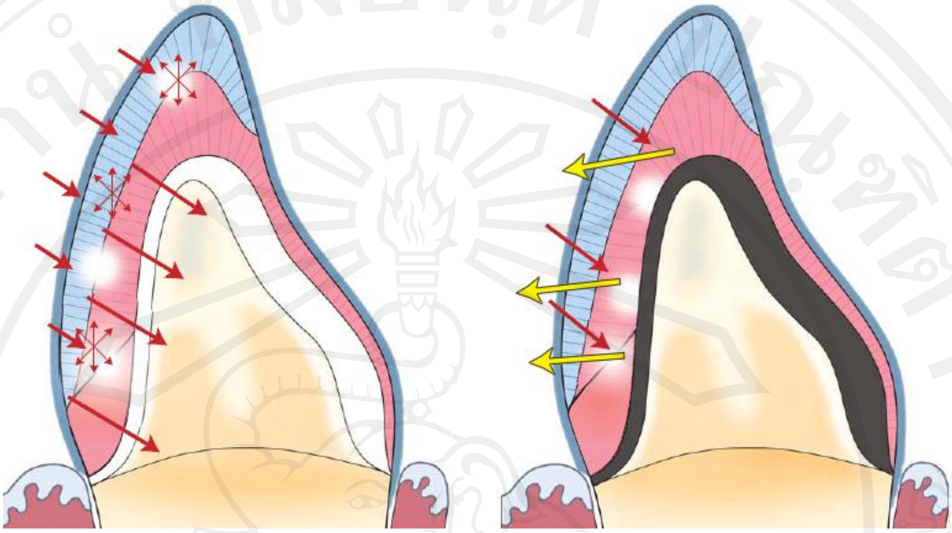

Fig. 2.9 In all-ceramic restoration, incidental light is transmitted and partially diffused through. On the other hand, when entering a PFM restoration, light is primarily reflected [45]**.**

Why is all-ceramic restoration interesting?

As people retain their teeth for much longer than in the past, the need for esthetically acceptable restorations is continuing to increase. Dental applications add esthetic requirements (color, translucency) to the mechanical specifications. White to ivory color gives a clear advantage for oxide ceramics versus metals, which is the reason why research and development are nowadays directed towards metal-free dental prosthetic restorations. Indeed, metal-free restorations preserve soft tissue color more similar to the natural one than PFM restorations. Moreover, ceramics do not suffer corrosion and/or galvanic coupling as it can be observed for metals. The clinical demand for all-ceramic restoration is increasing and ceramics are becoming important restorative materials in dentistry [32]. The other change that has occurred in the use of all-ceramic restorations has been societal attitudes concerning esthetics. Before the early 1980s, people in the entertainment industry were primarily the only patients who requested elective esthetic dental procedures [46]. One of the most significant of these changes occurred in 1983 when Horn [47] and Calamia [48] independently introduced acid-etched ceramics to create the bonded porcelain veneer, one of the most successful restorations when bonded primarily to enamel. With the advent of dentin adhesives in the early 1990s, porcelain restorations with significantly higher bond strengths than those that had been available previously became possible [49]. This prompted many practitioners to forego metal-ceramics and use bonded ceramics in clinical situations in which they had never before been used-sometimes successfully and sometimes unsuccessfully. A challenge still exists in that the dentin/adhesive bond is not as durable or predictable as the enamel/ adhesive bond [50]. This is reflected in the growing use by dentists of restorative procedures using ceramics. Ceramic have been advocated as material of choice for matching the natural teeth. The ability to blend a porcelain crown with its natural counterpart involves consideration of size, shape, surface texture, translucency, and color. Major strides in technology permitting routine use of all-ceramic restorations are the improvement and scientific innovations in the ceramic materials themselves [51].

Modern all-ceramic systems can be categorized into many groups depend on criteria to classification e.g. material or process. Leucite-reinforced feldspar glass ceramics are interesting material of choice due to high translucency, fluorescence, and opalescence. In according to esthetic results, the strength of leucite-reinforced feldspar glass is generally acceptable restorations.

2.2 Leucite

2.2.1 Composition and structure

Leucite is a naturally occurring potassium alumino-silicate that has a corner linked four and six-member rings of SiO_4 tetrahedral, forming the structure of a (Si, Al)-O framework silicate. Within the framework, two different cationic sites are existed. The larger site contains 16 positions, coordinated by 12 of oxygen, organized in line with channels, and formed by six-member rings. The second site contains 24 positions, coordinated by six of oxygen, although only 16 are filled [18]. The larger sites are usually occupied by potassium, rubidium or cesium ions, and smaller sites by water molecules or left vacant. Low temperature leucite is known to have a tetragonal structure which is similar to the high temperature cubic structure. Both cubic and tetragonal leucite contain 16 ($KAlSi_2O_6$) in the unit cell, with potassium ions occupying the center of channels aligned in parallel rows to the channel axes in cubic leucite. Around 605–625˚C phase transformation occurs from cubic to tetragonal leucite [18, 51]. At lower temperatures the potassium ions are too small to fill the cavities in the cubic structure and are moved away from their positions [52]. There is a collapse of the framework about them resulting in a change in symmetry and strain induced crystal twinning [53]. When a cubic leucite single crystal inverts to the tetragonal form, a complex twin develops. All six planes of the cubic form [54] may become twin planes in the tetragonal phase (point group 4/m) [55]. The crystal structure of tetragonal leucite, a = 13.09 Å, c = 13.75 Å, space group $I4_1/a$ [53], can be derived by displacing the cubic structure (some atoms must be shifted as much as l Å). There is no (Si, Al) order. The K atoms are coordinated by six oxygen at the average distance of 3.01 Å, six others being at ~3.7 Å. Cubic leucite these values are 3.35 and 3.54 Å; this is the most striking difference between the crystal structures [52]. Leucite undergoes phase transition, also described by Wyart [56], from a cubic phase (space group *Ia3d*) stable above 630˚C, to a tetragonal one (space group *I4$_1$/a*) stable at lower temperature. This polymorphic inversion was investigated in detail by Faust [53], who also listed previous studies of the problem. Recently, Peacor [57] refined the structure of the cubic phase of leucite at high temperature. The same author pointed out the difficulty of obtaining a suitable single crystal of the tetragonal phase due to the fine twins which always develop in tetragonal leucite during its inversion from the high temperature cubic.

Palmer et al. [58] found that transformation involves not only a ferroelastic distortion (giving rise to lamellar twinning and split diffraction spots), but also a “spontaneous volume” change. The order parameter (Q_{Eg}) describing the ferroelastic distortion corresponds to the transition *Ia3d→I4$_1$/acd*, and is coupled to the order parameter for the volume anomaly, Q_{T1g} (which corresponds to the transition *Ia3d→I4$_1$/acd.* The volume change is achieved by a crumpling of the {111} structural channels, which occurs in conjunction with an off-centering of K-ions, perpendicular to the channel axis (Fig. 2.10). Leucite has attributes of both a framework/cage structure, and a superionic conductor. The structural topology is an inter-connected array of $(A1,Si)O_4$ tetrahedra, linked to form 4-fold, 6-fold and 8-fold rings. The large cations (potassium) reside between 6-fold tetrahedral rings, on “W” sites, along structural channels which run continuously parallel to {111} (Fig. 2.11).

The 6-fold rings (of which two distinct types occur) are highly distorted in the low-temperature structure, and form 'bottlenecks', constraining the mobility of the K-ions. The {111} channels do not intersect, but pairs of channels are interconnected via side-channels (comprising 8-fold tetrahedral rings) parallel to {110} and {101}. Each K-ion sits at the intersection of three such side-channels (Fig. 2.10), and so remains relatively loosely bound despite distortion of the {111} rings. In the cubic phase the potassium are even more loosely-bound, and in X-ray structure refinements the thermal ellipsoids are markedly anisotropic [52]. Since K^+ is the only effectively mobile charge carrier in the leucite structure, its behavior has a direct influence on the overall dielectric properties [58].

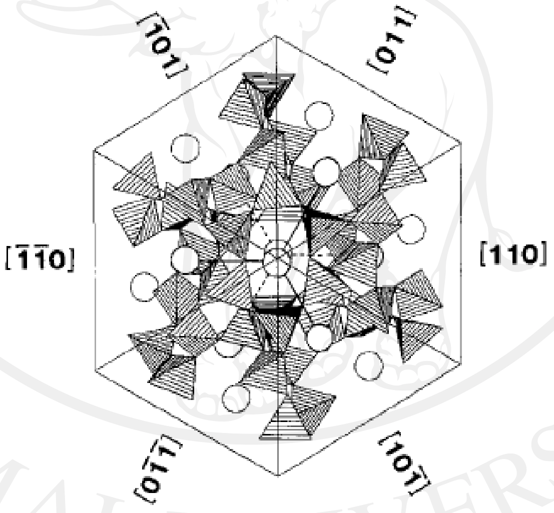

Fig. 2.10 The unit cell of tetragonal leucite (23˚C) viewed parallel to $\{1\bar{1}1\}$. The potassium atoms (spheres) reside along non-intersecting {111} channels; such channels are interconnected via side channels perpendicular to the main channel axis (shown as *lines* radiating from the central K atoms to neighbouring K atoms in adjacent channels; the distances between such K atoms are approximately 4.7 Å). Directions of the side channels are indexed [58].

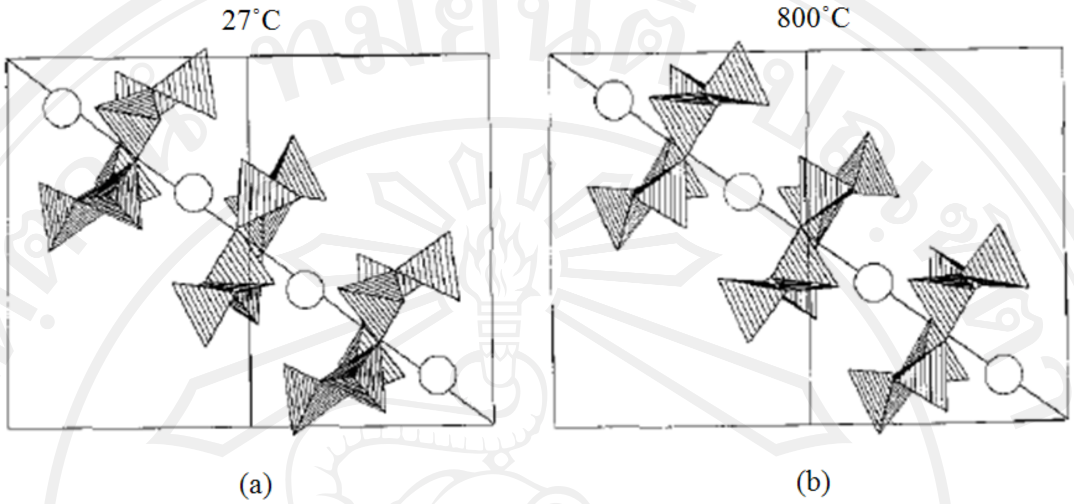

Fig. 2.11 View parallel to {110} showing the arrangement of potassium atoms and the six-fold tetrahedral rings along the {111} direction. (a) Below T_C, the potassium atoms (spheres) are off-centered with respect to the channel axis *(diagonal line).* (b) At 800˚C, in the cubic phase, the potassium atoms are aligned parallel to the *(triad)* channel axis, and the rings assume an undistorted profile. The average distance between the potassium ions parallel to this axis is approximately 6 Å [58].

2.2.2 Leucite reinforce dental porcelains

Dental porcelains are a desirable restorative material for oral rehabilitation because of its esthetic realism, resistance to degradation in the oral cavity, biological compatibility, and a coefficient of thermal expansion (CTE) that is similar to that of tooth structure. Serving as a strengthening and toughening agent, leucite is one of the most important components of dental porcelains. Leucite glass-ceramics can be produced by controlled crystallization of a glass via heat treatments [59]; the addition of synthetic leucite to powdered glass [60], and the blending of a high expansion leucite containing frit with a low expansion porcelain frit [12]. Leucite is mineral formed by the incongruent melting of feldspar, and it is used in the manufacturing of many dental porcelains. The composition of porcelain can be delineated in the tri-axial system feldspar-quartz-clay mineral substance. They can also be drawn in the ternary- phase diagram K_2O-Al_2O_3-SiO_2 (Fig. 2.12). Depending on the composition, feldspars can be heated to form a eutectic mixture of leucite and liquid according to the K_2O–Al_2O_3–SiO_2 ternary-phase diagram [65] (Fig. 2.12). The crystallization of leucite has also been achieved in these glasses by changes to the compositional ratios and an increase in K_2O content, together with the addition of suitable nucleating agents [66]. Significant crystallization was thought to be related to a minimum 1 wt% CaO and at least 12 wt% K_2O content in the glasses. Leucite is produced in situ in the porcelain frit through the incongruent melting of potassium feldspar to form leucite plus a more siliceous melt.

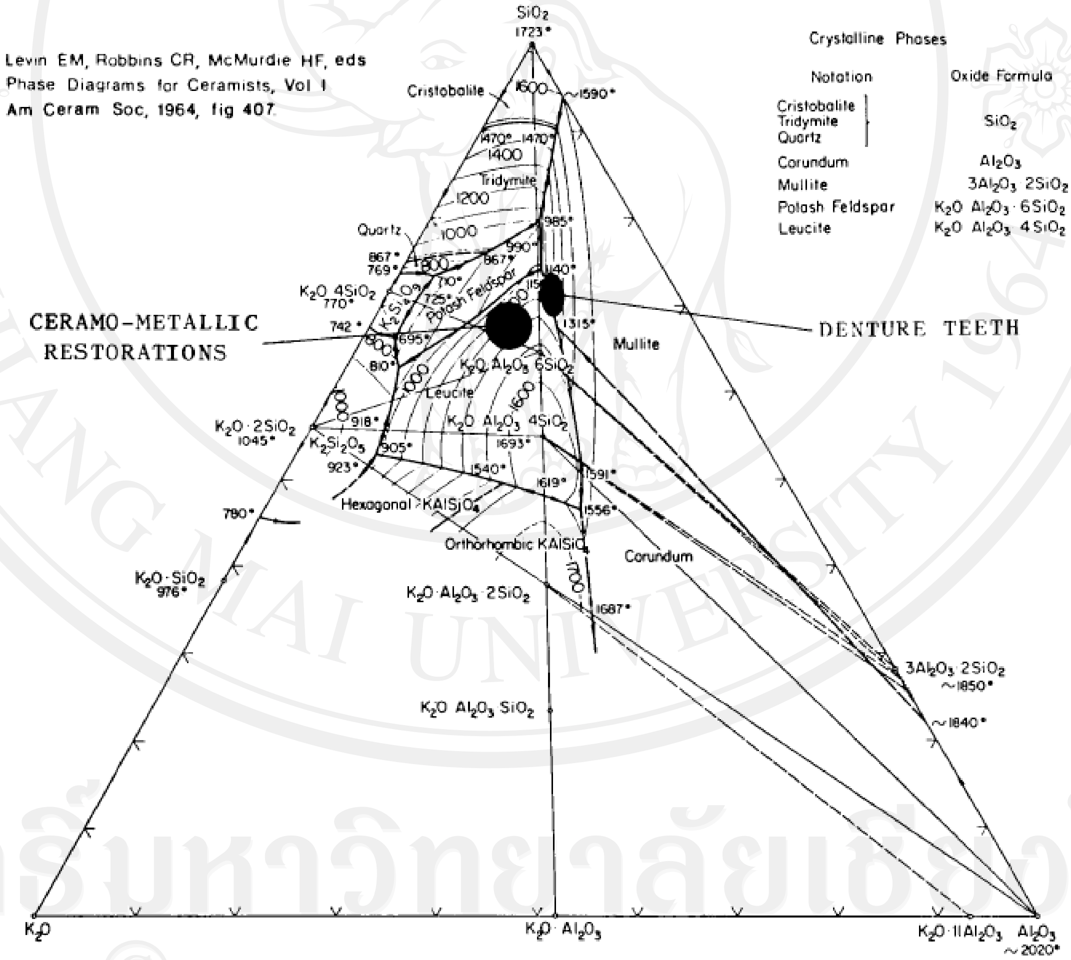

Fig. 2.12 Position of feldspathic ceramic bodies for denture teeth and for ceramo-metalic restorations in the ternary-phase diagram K_2O-Al_2O_3-SiO_2 [63]. Phase diagram reprinted by permission of American Ceramic Society.[64].

When the melt is cooled to room temperature, the result is leucite particles embedded in a glass matrix. Leucite, however, has been observed to convert to the sanidine ($KAlSi_3O_8$) polymorph of feldspar during certain translucent to opaque. However, sanidine does not appear when the porcelain is heated to 980˚C, since sanidine is metastable in the temperature range 500-925˚C. The precipitation of sanidine has been reported as well upon isothermal heat treatment of conventional feldspathic porcelains for metal-ceramics [65, 66].

Leucite-based frits have been since the early 1960s in the manufacture of materials for metal-ceramic application. Leucite containing porcelains are used in dentistry to fabricate dental restorations in order to achieve metallic substructures. Most dental porcelains for metal-ceramic restorations contain leucite as the major crystalline phase. Leucite was first introduced into dental porcelain compositions to match the thermal expansion behavior of the metal substructure when cooled. The high-temperature form is cubic and the low-temperature form is tetragonal with a transformation temperature of 625˚C [52]. The CTE of the cubic leucite is 3 x 10^{-6}/˚C from 625˚C to 900˚C, whereas, for tetragonal leucite, CTE is 25 x 10^{-6}/˚C from room temperature to 625˚C [36]. The high thermal expansion of leucite is the result of both an intrinsically high α value (22 x 10^{-6}/˚C) and the tetragonal-to-cubic phase transformation [9]. The high expanding leucite raises the bulk porcelains thermal expansion (α) of dental porcelain to a required level where it is compatible with metal substrate. The crystallization or introduction of a high expansion tetragonal leucite phase into a base glass is advantageous to increase its expansion coefficient to a level sufficient to allow efficient bonding to metals. The difference in thermal expansion between the tetragonal leucite crystals and the glassy matrix (8.6 x 10^{-6}/˚C) also provides tangential compressive stresses around the crystals that are thought responsible for significant strengthening in feldspathic dental porcelain [13]. More recently, leucite has been used in all-ceramic materials, not for thermal compatibility, but as a reinforcing material for all-ceramic restorations [67].

Improvements in ceramic technology have taken the form of novel processing techniques. This, along with patient demands for superior esthetics, has led to renewed interesting all-ceramic-dentistry. Many researchers have interested in development of all-ceramic core. During the last decade, material for all-ceramic core has been used a wider variety of crystalline phases as reinforcing agent, such as leucite, litium disilicate, fluoro-apatite, alumina, and zirconia (Fig. 2.13). Leucite-reinforced feldspathic porcelains have been superior esthetic compare to other crystalline reinforced porcelains. It can be processed into dental prostheses by many mechanisms, including, sintering, heat pressing, and computer aided design and machining [68-70].

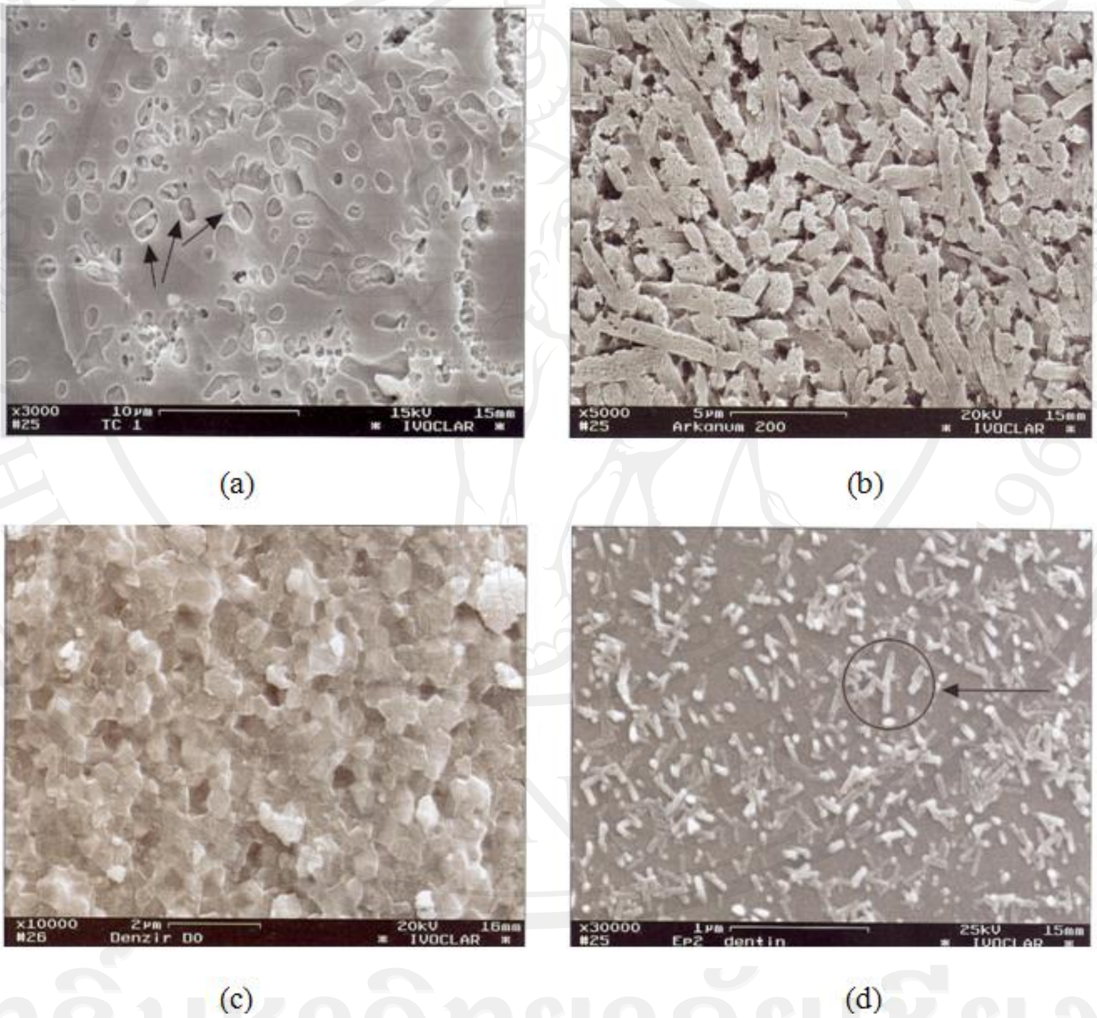

Fig. 2.13 Micrograph of crystalline phase reinforced porcelains; (a) leucite, (b) lithium disilicate, (c) zirconia, and (d) fluoro-apatite [71].

2.2.3 Phase transformation of leucite reinforce dental porcelains

Leucite is a potassium alumino-silicate and undergoes a crystallographic transformation from tetragonal to cubic at 625˚C [52]. This inversion is associated with a marked change in the crystalline lattice constants. Previous studies [9, 65] have shown that the lattice constants for tetragonal leucite at room temperature were a = 13.197 ± 0.013 Å and c = 13.819 ± 0.016 Å. In feldspathic dental porcelains, the transformation into cubic leucite was reported to start at temperatures as low as 400˚C and lead to a 1.2% volume increase of the unit cell with a lattice constant a = 13.565 Å. During the transformation from tetragonal to cubic, the unit cell of tetragonal leucite expands along the a-axis and contracts along the c-axis. Leucite transformation leads to reversible 1.2% discontinuous volume change, from low temperature tetragonal to the high temperature cubic leucite starting at 400˚C, in respect to crystallized feldspathic glasses. The thermal expansion change from tetragonal leucite to cubic leucite is associated with the volume increase [9]. The advantage of high expansion tetragonal leucite phase into matrix glass is to increase its expansion coefficient and allow efficient bonding to metals. In addition to the large thermal expansion mismatch between the tetragonal leucite crystals (22 to 25 x 10^{-6}/˚C) and the glassy matrix (8 x 10^{-6}/˚C) also provides tangential compressive stresses around these crystals when they are cool (Fig. 2.14). These stresses can act as crack deflectors and contribute to increase strengthening in feldspathic dental porcelains significantly [72]. The temperature range of low-high leucite transformation is generally reported to be 605˚C - 625˚C [52], although Faust found literature values for the lower and upper limits, respectively, of the leucite transformation range as low as 433˚C to 560˚C and as high as 684˚C to 714˚C. Mackert et al. [65] found by high-temperature X-ray diffraction that small proportion of the leucite crystallites in dental porcelain transformed from the tetragonal to cubic form at temperature as low as 400˚C, while transformation of all crystallites to the cubic form did not occur until 600˚C.

Usually, the high-temperature form, cubic leucite, will transform to a tetragonal leucite at around 625˚C when cooled [52]. Only when a larger-size cesium cation or rubidium cation replaces the potassium cation can the cubic leucite be stabilized to room temperature [73, 74]. Previous work [75] showed that the high-temperature

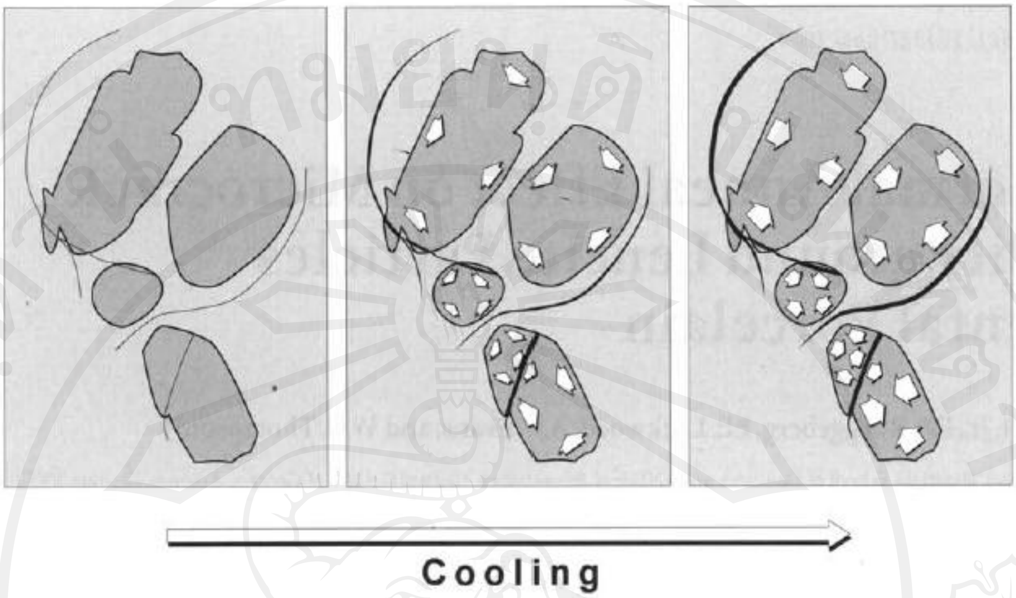

Fig. 2.14 Schematic of microcracks during cooling of porcelain from the glass transition temperature to room temperature. As the porcelain cools down from the firing temperature, the leucite contracts more than the surrounding glass matrix, owing to its higher coefficient of thermal expansion and the cubic-to-tetragonal phase transformation. At some temperature below the glass transition temperature of the glass matrix, the walls of the cracks around the leucite particles separate due to the contraction of the leucite particles [76].

form of leucite could be stabilized in feldspathic dental porcelain by the addition of cesium carbonate to the starting composition. Although, the addition of cesium was effective in stabilizing the cubic polymorph of leucite to room temperature, the result of this stabilization was detrimental to the flexural strength of the leucite-reinforced porcelain and reduced its crack deflection ability. Stabilized leucite has a lower overall contraction during cooling because of its lack of a cubic-to-tetragonal transformation and its lower intrinsic thermal expansion coefficient. These factors combine to produce smaller residual tangential compressive stresses around the stabilized cubic leucite crystals than around tetragonal leucite. Apparently, the development of these tangential compressive stresses around the leucite crystals is responsible for a significant amount of strengthening of feldspathic dental porcelains [72]. The dental porcelains are expected to be at a molten state at temperatures about

1200˚C or higher. Therefore, the absent formation of leucite at temperatures of 1300˚C or higher is due to the dissolution of leucite particles into the molten glass followed by subsequent fast cooling, which suppresses the re-precipitation of leucite particles in the cooling process [77].

The overall volume increase of the unit cell is associated with a change in the thermal expansion coefficient from 22.3 x 10^{-6}/˚C over the range 25 to 400˚C for tetragonal leucite to 21.5 x 10^{-6}/˚C over the range 400 to 700˚C for cubic leucite [9]. However, Hermansson and Carlsson [78] reported a value of 11.7 to 12.8 x 10^{-6}/˚C over the range 25 to 600°C for cubic leucite stabilized to room temperature. Mackert [51] showed that microcracks develop in leucite containing dental porcelain when cooled. The microcracks are located within the leucite crystals and in the glass matrix around the particles. Crystal and matrix microcracking have been linked to the cubic to tetragonal leucite transformation when the unit cell expands in the c-axis and contracts in the a-axis, with a resultant anisotropic stress distribution [79].

2.2.4 Content and size of leucite reinforce dental porcelains

Leucite reinforced all-ceramic have higher leucite content than conventional feldspathic porcelains that are designed for fusing to metal. Many of processing heat treatments used in fabrication of metal ceramic restorations are known to induce crystallization of additional leucite in conventional feldspathic porcelains [5]. Typical leucite volume fractions for leucite containing dental porcelains vary between 17-45% of tetragonal leucite in a glassy matrix [2, 67] with biaxial flexural strengths for leucite reinforced frit materials varying from 56 to 137 MPa [80]. Many researchers have been demonstrated multiple firings, isothermal heat treatments and cooling of dental porcelains necessary for restoration fabrication can modify this content [5, 81, 82]. Slow cooling and post-soldering treatments cause increases in leucite content [81]. Porcelains are capable of precipitating additional leucite during slow cooling following a normal firing schedule. These results also demonstrate that some porcelain compositions are more susceptible than others to the crystallization of additional leucite during slow cooling. Several possible mechanisms for the thermal expansion coefficient of dental porcelain have been proposed, including de-coupling and re-coupling of leucite particles from the glass matrix and relaxation of trapped excess volume during cooling or annealing at temperatures close to the glass transition temperature [51]. Mackert and Evan [81] determine whether changes in leucite content of a dental porcelain resulting from thermal treatments. A significant positive relation was obtained between leucite volume fraction and duration of optimal heat treatment temperature.

The microstructure of a ceramic material is known to strongly affect crack propagation and its mechanical properties. In this regard, it has been demonstrated that dental porcelains with higher amounts of leucite are more resistant to fast crack propagation, and have higher fracture toughness due to the phenomenon of crack deflection around leucite particles [83]. Therefore, it is expected that the presence of leucite in the glassy matrix of porcelains will also hinder slow crack propagation. However, leucite content of dental porcelains does not influence their susceptibility to slow crack growth in saliva test environment [84]. Other factors that may influence crack growth of porcelains in the clinical situation are: (a) moisture from the luting cement; (b) fatigue stresses from masticatory forces [85]; (c) handling and design of the restoration; and (d) thickness of the restoration [86]. Moreover, literature reported that there was no significant relationship between increasing additions of leucite and higher mean biaxial flexural strength values [76]. Leucite content in borosilicate and feldspar glasses explored above 20 wt% resulted in reductions in bending strength, which were explained by the large mismatch of thermal expansion and the degree of microcracking that was not present in compositions with smaller additions of leucite [87].

The nature, amount, and particle size distribution of the crystalline phase directly influence the mechanical and optical properties of the material [88, 87]. Current commercial production methods produce dental porcelains with larger leucite crystal sizes (~5-10 μm) or clusters [2, 30, 66]. Dendritic leucite morphology is also present in some instances [89]. The thermal expansion mismatch between the leucite crystals and the glass matrix developed during leucite transformation often causes signs of microcracking around these larger (~10 μm), non-uniform leucite crystals and clusters [2, 89]. Microcracking has been shown to be crystal size dependant. It can be minimized by a reduction in the mean leucite particle diameter to less than 4 μm [90].

The presence of large particle inclusions or particle agglomerates above a critical size have been associated with extensive microcracking in the glassy matrix [89] producing stress raisers larger than the inherent flaws, as the energy for a growing flaw is potentially provided by the elastic stored energy in the particle and the adjacent glassy matrix [25]. The inclusion of small rather than larger particle sizes into a glassy matrix have produced minimal microcracking and flexural strength improvements in different composite systems [31].

Generally, a fine grained microstructure is desirable to improve the mechanical strength [91], wear [92, 93] and optical [94] properties of the dental porcelains. The fine grained can improve mechanical properties compared to commercial dental porcelains materials [95]. A number of studies have shown that fine (1 μm) leucite crystals and uniform leucite distribution in the glassy matrix may produce less microcracking, reduce the susceptibility of the glassy matrix to fracture, and give more ideal flexural strength properties [30, 54]. Cattell et al. [95] who confirmed that fine leucite crystals, tabular platelets and minimal matrix micro-cracking were found in ceramics with a more uniform leucite distribution which were associated with a significant increase in the biaxial flexural strength and reliability. The vitro wear studies of ceramic material against human enamel suggest that a reduced crystal size and crystallization produces a smaller amount of enamel and ceramic loss [92, 93]. Moreover, the match between the refractive indices of the crystalline phase and glassy matrix is a key factor for controlling the translucency of the porcelain. [79]. Translucency may be achieved with a very fine (submicron) grain size and low porosity content (less than 1%), which has attracted much attention due to its special properties [32].

The fine grained leucite is obtained from controlled crystallization of leucite via heat treatments [3, 4, 95]. Several authors [96, 97] have illustrated dramatic variations in crystal sizes in the same glass composition, depending on the applied nucleation and growth heat treatments. The volume fraction, crystal size and morphology of the crystalline phases are dependent on the original glass composition. The stoichiometry of the crystal phases and crystallization is related to optimal heat treatment times and temperatures. Optimization of the microstructure by producing a fine microstructure and controlling its distribution through the correct heat treatment parameters may be extremely advantage. If adequate strength can be maintained at a lower crystalline content there is also the potential benefit of reduced opacity and increased low at lower processing temperatures, which could influence the fit and esthetics of the finished ceramic restoration. A more controlled crystallization regimen of the glass may therefore be a useful route to control the leucite crystal size, volume fraction, and morphology of these materials, which can influence the mechanical glass-ceramic properties. In summary, the mechanical properties of Glass Ceramics are believed to be greatly influenced by:

- particle size of the crystalline phase
- volume fraction of the crystalline phase
- interfacial bond strength between phases
- differences in elastic moduli
- differences in thermal expansion.

The controlled crystallization of glasses has also been employed [59]. Controlled crystallization of glasses generally involves the melting, forming and cooling of glasses to form appropriate shapes or powders that are subsequently reheated to promote crystallization, via a nucleation and growth process [97]. During a subsequent heat treatment controlled crystallization, occurs with the nucleation and growth of internal crystals. The controlled crystallization of the glass results in the formation of tiny crystals that are evenly distributed throughout the glass. The number of crystals, their growth rate and thus their size are regulated by the time and temperature of the heat treatment. A high rate of nucleation and low growth rate is required to achieve a fine grained ceramic since many more sites are provided for crystal growth [97]. The outstanding attention the nanostructure material have recently drawn, stem from their useful mechanical, physical, and optical properties. Meanwhile, further improvement in the properties is expected by decreasing the grain size to nano-scale. Although the sinter ability of nanoparticles is superior to fine particles due to higher sintering stresses, the more intensive grain growth during densification deteriorates the advantages of nanostructure bulk materials [98]. In the recent times the interest of dentists, dental technicians, and patients in all-ceramic materials has rapidly increase as stronger and tougher materials are developed and commercialized along with novel processing technologies. The grain growth can be controlled by two approaches: one is to prohibit grain growth by addition or dispersion of a second phase particles [99]; the other is to control grain growth by a novel processing method.

In connection with this, Chen and Wang [6] have developed a new technique called two-step sintering (TSS) which is a promising approach to obtain nano-grained ceramics. The key elements in this method are (i) heating to a high temperature (T_1) to allow copious nucleation; (ii) decreasing the temperature (T_2) to conduct sintering without any grain growth at the lower temperature. TSS has been successfully to obtain nanoceramics such as Y_2O_3, TiO_2, ZrO_2 and Al_2O_3. [6, 100-102]. So far, Cattell et al. [4] studied effect of tempering time on size of crystalline leucites using two-step sintering technique. They successfully produced uniform distribution of fine leucite crystals in glassy matrix with optimal tempering time (60 min); moreover, longer tempering firing time has been found to relate with an increasing size. However, they could not reach the nanocomposites structure. In recent year, Sanitnapapong et al. [7] demonstrated that the two-step sintering technique together with 20 wt% ZrO_2 additive has considerable potential for the production of leucite/porcelain ceramic nanocomposites. Moreover, they found that the highest leucite content is performed when the firing condition was 1040˚C for 5 min then tempering at 940˚C for 90 min. In this study, the two-step sintering (TSS) concept was adopted for the sintering of leucite-reinforce dental porcelain ceramics with various amount of ZrO_2 additives. Therefore, crystallization of the experimental ceramic to form nano-leucite dental porcelain or a leucite composite system should also be possible if the correct ZrO_2 contents are applied.

2.3 Zirconia

Prior to 1975, pure zirconia was of very limited interest as a structural or engineering ceramic, and its use was restricted to refractory applications [103]. An excellent review by Chevalier, evaluating the future of zirconia as a biomaterial has recently been published [104]. Since among bioceramics, particular attention has been paid to zirconia-based bioceramic owing to its outstanding biocompatibility, wear resistance, high toughness, chemical inertness, low thermal conductivity, and superior esthetic properties [105, 106], which has become a hot topic of research in the biomaterial region [107]. The development of advanced dental material technologies has recently led to the application of zirconia-based ceramics in dentistry. Therefore, zirconia becomes increasingly popular as a dental restorative material, under various forms and with a wide range of processing conditions.

2.3.1 Composition and structure

Zirconia exists in three major phases: monoclinic, tetragonal, and cubic (Fig.2.15). The monoclinic phase is the low temperature, stable phase. Pure zirconia is monoclinic at room temperature, and this phase is stable up to 1170˚C. Above that temperature, it will transform into the tetragonal intermediate phase, which may be stabilized at room temperature dependent on the concentration of the stabilizing oxide added and the grain size of the zirconia particles. At a temperature of 2370˚C, zirconia transforms into a cubic phase, which is stable only at very high temperatures [108]. In pure zirconia ceramics, without stabilizing oxides, reverse tetragonal to monoclinic phase transformation can occur during cooling. The tetragonal to monoclinic (t→m) phase transformation occurs at a temperature around 950˚C and results in a 4% increase of volume that causes compressive stresses [108]. In phase transforming materials, the magnitude of the compressive stresses is further improved by the t→m phase transformation [109]. The compressive stresses may counteract tensile stresses acting at the crack tip and thus increase the strength of a given ceramic [110]. The reverse tetragonal-to-monoclinic transformation can also be initiated by stress around a crack tip, with volumetric expansion. This transformation is beneficial because it can result in partial closure of a crack (transformation toughening) [111]. In addition to the transformation toughening associated with the t→m transformation around advancing cracks, other mechanisms, such as crack deflection, crack bridging and the presence of microcracks, may also enhance the toughness. The remarkable mechanical properties of zirconia, already exploited in several medical and engineering applications, are mainly due to its transformation toughening. It also has low thermal conductivity, high thermal expansion coefficient, phase stability to 1400˚C, and good erosion resistance [107].

2.3.2 Zirconia reinforced ceramics

ZrO_2-containing glass-ceramics can be produced by bulk crystallization of ZrO_2-containing glasses [88, 95, 112, 113], or by sintering and crystallization of pressed mixtures of glass and ZrO_2 powders [114]. Zirconia particles are frequently employed as a toughening agent for other ceramics, and these zirconia toughened ceramics (ZTCs)

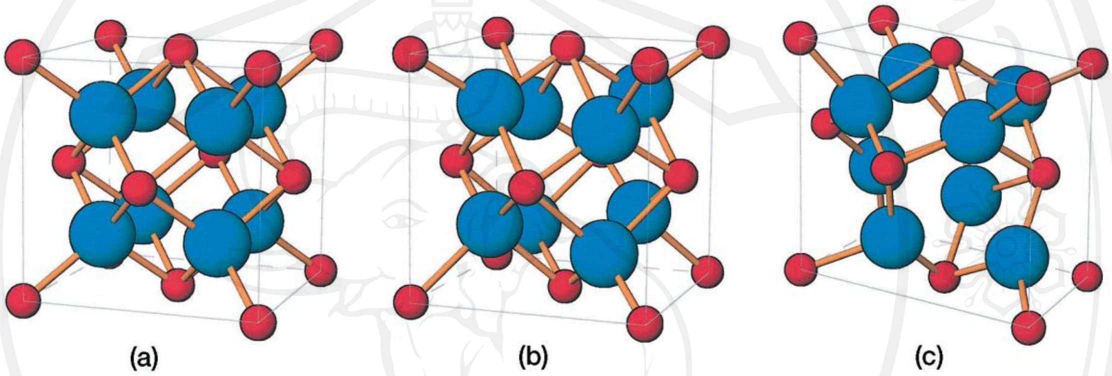

Fig. 2.15 Schematic representation of the three polymorphs of ZrO_2: (a) cubic , (b) tetragonal, and (c) monoclinic [115].

have received great attention in the last two decades [115]. Ceramics dispersed with ZrO_2 as a second phase have been extensively investigated to improve the mechanical properties of alumina, dental porcelains, and glass-ceramics [114]. The fracture toughness of ceramics was increased from 1.75 to 2.4 MPa $m^{1/2}$ with addition of m-ZrO_2 up to 10 vol% [116]. The previous study demonstrated that adding both t-ZrO_2 and m-ZrO_2 particles can significantly enhance the mechanical properties of alumina ceramics. A compressive surface layer is formed on the machined surface due to the volume expansion accompanied by the t→m transformation [113]. The use of metal oxides containing ZrO_2 as doping agent for glass ceramic is known in the art. It is preferred that the doped leucite glass ceramic according to invention contain nanoscale metal oxide in amount 1-80% by weight (relative to the total weight of doped leucite glass ceramic), especially 30-70% by weight, particularly preferably about 60% by weight [117]. These doped leucite glass ceramics can be made by any suitable method, on the basis of the corresponding amount of leucite glass ceramics and nanoscale metal oxide powder. The dope leucite glass ceramics according to the intervention with highest bend strength are obtained with 60% by weight of unstabilized ZrO_2 as metal oxide powder. Due to high bend strength and fracture resistance, the doped leucite glass-ceramics according to the intervention are very well suitable as dental material. Moreover, they exhibit a good resistance to thermal shock. The above mention properties mean that this material is also used as dental product. It is possible to create preferred dental products as root restoration such as tooth root construction or root post [117]. However, Tuan et al. [113] found that 20% ZrO_2 reinforcement in ceramics is strong enough for fabrication of anterior crown. Moreover, second phase particles in ceramic composites can inhibit grain growth and lead to a relatively fine microstructure. It is known that the grain growth behavior of the ceramic matrix can be controlled by adding various amounts and types of oxide additives [118]. Several authors demonstrated that zirconia influences the crystallization by hampering crystal growth. With the increasing ZrO_2 content, the crystals become smaller [8, 119].

2.4 Ceramic Nanocomposites

Nowadays, it is difficult to avoid the word “nano” in a scientific paper. However, disregarding this somewhat despicable consideration, one must admit that nano-structured ceramics may offer some specific improvements versus micro-structured ones. The composite can expect higher hardness resulting in better wear behavior, specific toughening mechanisms that may improve crack resistance, and better translucency (potentially interesting for dental restorations). The improvement of diverse physical properties has already been demonstrated for variety of nanophase and nanocomposite ceramics obtained in the past decade [120]. The fabrication of nanopowders into fully dense components that retain a nanocrystalline grain size has lagged behind powder synthesis and characterization. In part, the gap between powder synthesis and fabrication is related to an incomplete theoretical understanding of the mechanisms and consequences of densification and sintering when grain interfacial regions dominate. Equally relevant is the incomplete understanding of the particular experimental conditions that yield high-density compacts without microstructural coarsening. The available experimental work in this area clearly demonstrates that the conditions for densification and sinterability of nanocrystalline materials is system specific and is not readily deduced from theory alone at the present time.

Due to the difficulty in producing ceramics with nanocrystalline-matrix grain sizes, most of the research on nanoscale effects in ceramic composites has been on composites with microcrystalline matrices and nanocrystalline second phases [121]. Certain toughening mechanisms in microcrystalline ceramic systems have been reasonably well developed and investigated; the essence of them is summarized in the following sections.

2.4.1 Ductile-Phase Toughening

The addition of certain ductile phases (metals) to ceramic matrices has proven to be an effective toughening mechanism. The ductile phase can lead to toughening of the composite through two distinct mechanisms [122]. The first is through ductile yielding in the process zone of a propagating crack to increase intrinsic toughness. The stress field around the crack tip can be relieved through adsorption of energy through the deformation of the ductile phase or blunting of the crack tip at a ductile particle (Fig. 2.16(a), (1)). The second manner in which a ductile phase can lead to toughening of a ceramic composite is by ductile bridging ligaments in the crack wake, increasing extrinsic toughness. This occurs when the crack tip propagates past a ductile-phase grain that then bridges the crack wake (Fig. 2.16(a), (2)) and must be pulled to failure (Fig. 2.16(a), (4)) or debond from the surrounding matrix (Fig. 2.16(a), (3)). These toughening effects should be applicable in nanocrystalline ceramic-matrix composites as long as the ductile-phase grain size is large enough to support plastic deformation. Pure nanocrystalline metals typically do not exhibit dislocation-mediated plasticity below grain sizes of 15-30 nm [123].

2.4.2 Fiber Toughening

The most common toughening mechanism associated with the incorporation of fibers into a microcrystalline ceramic matrix is fiber bridging [123, 124]. This toughening mechanism involves the bridging of the crack wake by the second-phase fibers (Fig. 2.16(b)). The toughening effect is achieved when the fibers either shed load from the crack tip while remaining intact (Fig. 2.16(b), (3)), the interface debond between the fiber and the matrix followed by pullout (Fig. 2.16(b), (2)), and/or the individual fibers fracture, followed by energy adsorption through pullout of the broken fiber (Fig. 2.16(b), (1)). These effects lead to increased extrinsic toughness. Another possible toughening mechanism is crack deflection, as seen in micro-crystalline fiber-reinforced ceramic composites [121]. When the fiber is of particular orientation (Fig. 2.16(b), (4)), crack propagation can be deflected away from the axis of the highest stress to the less-efficient orientation directed by the longitudinal orientation of the fiber. This leads to increased fracture energy through increased fracture surface area and lower driving forces due to the reduced resolved normal stresses at the crack tip as a result of the deflection of the crack tip away from the Mode I loading orientation*. This phenomenon will enhance the intrinsic toughness of the material. Both crack deflection and fiber bridging should be pertinent to nanoceramic composites, since neither method is inherently dependent on the matrix grain size.

2.4.3 Transformation Toughening

Transformation toughening has been investigated in ceramics containing zirconia as a second phase [127]. It relies on the transformation of zirconia from the tetragonal to the monoclinic phase under applied stress. This transformation occurs in the stress field around the crack tip (Fig. 2.16(c), (1)), and the resultant strain involved in the transformation locally relieves the stress field and absorbs fracture energy. Point (2) in Fig. 2.16(c) shows the resultant zone of transformed particles left in the crack wake. This will increase intrinsic toughness. The transformation toughening mechanism is directly affected by the stability of the tetragonal phase of the zirconia. The phase stability is dependent on dopant concentration, the grain size of the zirconia phase, and the testing temperature. Because of the fine balance of dopants and grain size, it is not clear whether transformation toughening will be a feasible toughening mechanism in ceramic nanocomposites. Bhaduri and Bhaduri [128] have produced a nano-nano composite of alumina and zirconia that exhibited a dramatic improvement in toughness without evidence of a phase transformation.

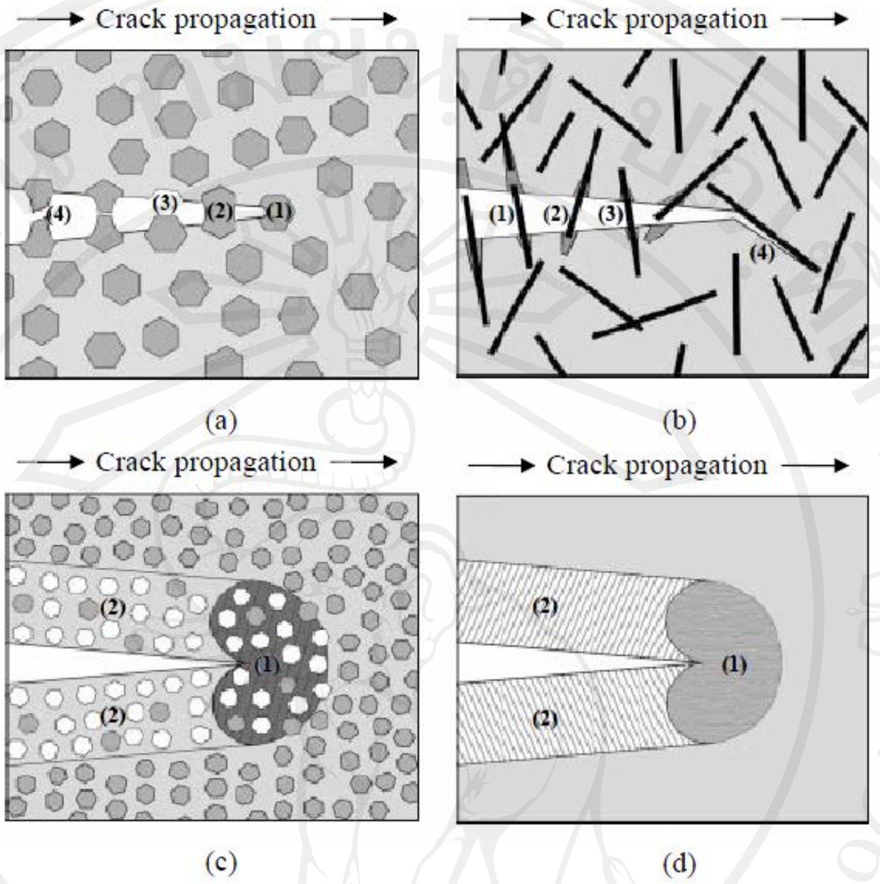

Fig. 2.16 Schematic illustrations of toughening mechanisms in ceramic-matrix composites: (a) ductile-phase toughening, (b) fiber toughening, (c) transformation toughening, and (d) microcrack toughening [125, 126].

2.2.4 Microcrack Toughening

Analogous to the tetragonal-monoclinic transformation behavior of zirconia, stress-induced microcrack formation represents an irreversible deformation phenomenon that is associated with energy dissipation and stress shielding. Microcracking is induced by the combined action of thermal residual stress and applied stress field at the crack tips. This can be observed in single-phase material (with an anisotropic thermal expansion coefficient) as well as in multiphase material (with different thermal expansion coefficients between the phases) [129, 130]. The

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*Mode I loading orientation: Tensile cracks fractures open slightly in direction perpendicular to crack surface [121, 125].

presence of microcracks deflects or branches out the main crack as well as shielding stress at the crack tip, increasing the intrinsic toughness. Fig. 2.16(d) shows the zone of microcracking at the crack tip (Fig. 2.16(d), (1)) as well the microcracks left in the crack wake (Fig. 2.16(d), (2)). When it is effective, microcrack toughening can increase the fracture energy of ceramics by 20-40%. Pure alumina, alumina reinforced with monoclinic zirconia [131], and SiC reinforced with TiB_2 [132] have shown toughening arising from this mechanism. The ability to apply the mechanism of microcrack toughening to composites with nanocrystalline ceramic matrices is still uncertain because of the dependence of the toughening on microcrack length, which is undoubtedly dependent on grain size, since microcracks are typically generated at grain boundaries.

In the effort to produce ceramic nanocomposites, the introduction of a second phase is helpful in two ways: (i) the second phase will prevent grain growth of the matrix to some extent; and (ii) toughening of the material can be achieved if the second phase is chosen with appropriate properties. Niihara et al. [133] classified the nanocomposites into four groups (Fig. 2.17(a)) based on matrix grain size and second-phase particle size. The first three types of nanocomposite fall into the micro-nano category, that is, nano-sized second-phase particles dispersed in a micro-crystalline matrix. The large majority of so-called nanocomposites developed to date are micro-nano composites, rather than nano-nano composites (where both the matrix and inclusion grain sizes are in the nanometer range). Kuntz et al. [134] propose that a true investigation into nanocomposites requires a reclassification such as that seen in Fig. 2.17(b). In this new classification, the matrix phase is continuously nano-crystalline while the second phase varies, leading to four nanocomposite types: the nano-nano type, the nanomicro type, the nano-fiber type, and the nano-nanolayer type:

- Nano-nano composite: both the matrix and second phase have equiaxed grains of less than 100 nm [121, 123];
- Nano-micro composite: nanocrystalline matrix and a microcrystalline second phase;
- Nano-fiber composite: whiskers or fibers incorporated into a nanocrystalline matrix [123, 124]; and

• Nano-nanolayer composite: nanocrystalline matrix and a grain boundary layer of a second phase [121].

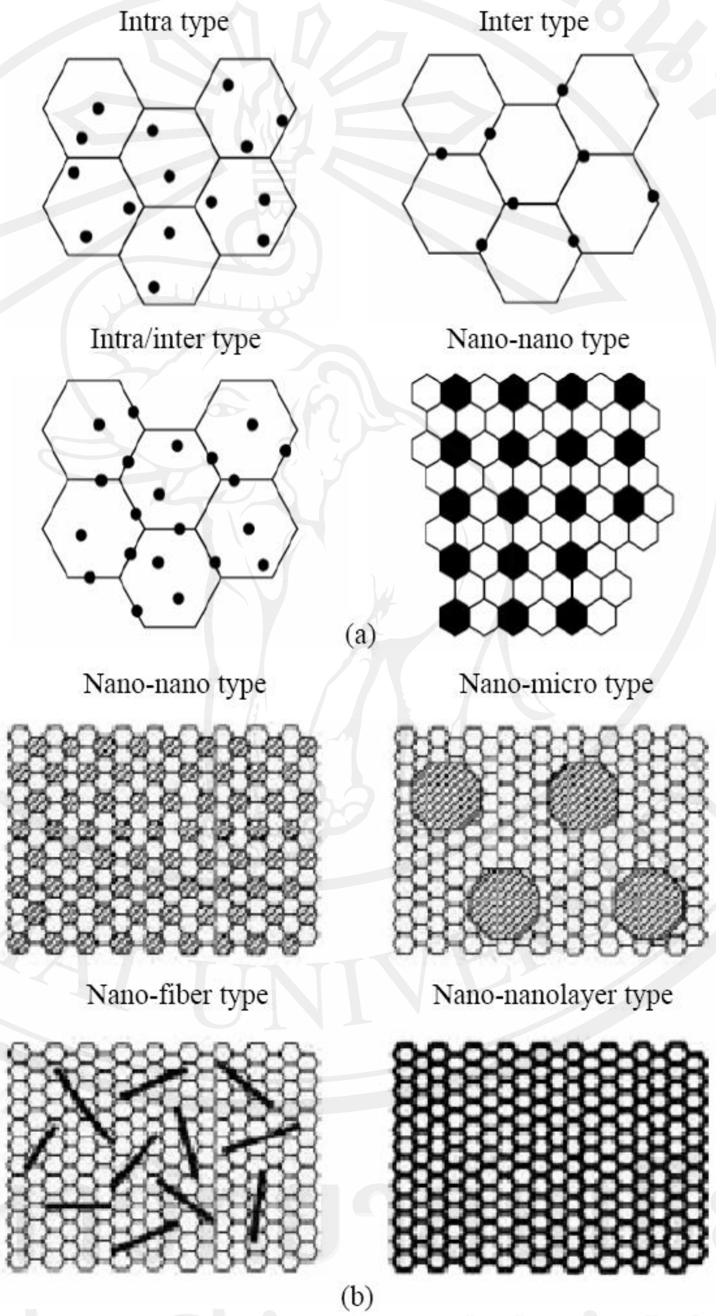

Fig. 2.17 (a) Niihara's classification [133] of nanocomposite types, based on matrix grain size and second-phase particle size. (b) A new classification Kuntz [134] in which the matrix phase is continuously nanocrystalline while the second phase varies, leading to four nanocomposite types.

Enthusiasm in developing micro-nano composites was triggered by Niihara's pioneering work in the late 1980s [135]. His group reported a significant increase in flexural strength, from 350 MPa to 1–1.5 GPa, accompanied by an increase in fracture toughness, from 3.5 MPa·m$^{1/2}$ to 4.8 Pa to 1–1.5 GPa, accompanied by an increase in fracture toughness, from 3.5 MPa·m$^{1/2}$, by introducing 5% SiC nanoparticles into microcrystalline Al_2O_3 [135, 136]. Since then, the research activity in this area has been very intense, and the new concept of adding metric nanoparticles has been introduced into various materials systems. Composite materials result from the joining of two (or more) different materials is more interested. While in the polymeric matrix composites the reinforcement is needed to improve the mechanical strength and stiffness of the unreinforced matrix, in the ceramic matrix composites the reinforcement is needed mainly to modify the fracture behavior, causing the composite to be less brittle than the parent ceramics [137, 138]. The enhancement of fracture toughness, in relation to the un-reinforced matrix, is due to a complex of matrix/reinforcement interactions, which causes cracks to deviate or branch, with certain fracture energy absorption. Crystalline phase-reinforced ceramics, in which matrix/reinforcement interactions cause the maximum energy absorption, show excellent bending strength and fracture toughness. Significant experiences have been conducted on the reinforcement of glass (and glass ceramics) with ceramic particles [139, 140]. The improvement in mechanical properties is mainly related to crack deflection, caused by the introduction of compressive residual stresses in the matrix, due to the thermal expansion mismatch between the phases. Crack deflection, as a toughening effect, is strongly dependent on the aspect ratio (ratio of length to width) of the reinforcing phase [141].

Although composite structures are not new for dental ceramics, the design of specific composition and microstructure using ceramic nanocomposite concept is a novel idea for the dental porcelain-based system. Thus, in this research project, it may be possible to fabricate a material that produces a nanostructure, which has been designed for a specific purpose of dental applications, e.g. to enhance physical, mechanical, and optical properties.