A Review of the Characteristics and Optimization of Optical Properties of Zirconia Ceramics for Aesthetic Dental Restorations

R. A. Shahmiri, O. C. Standard, J. N. Hart, C. C. Sorrell

Abstract—The ceramic yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) has been used as a dental biomaterial for several decades. The strength and toughness of this material can be accounted for by its toughening mechanisms, which include transformation toughening, crack deflection, zone shielding, contact shielding, and crack bridging. Prevention of crack propagation is of critical importance in high-fatigue situations, such as those encountered in mastication and para-function. However, the poor translucence of Y-TZP in polycrystalline form is such that it may not meet the aesthetic requirements due to its white/grey appearance. To improve the optical properties of Y-TZP, more detailed study of the optical properties is required; in particular, precise evaluation of the refractive index, absorption coefficient, and scattering coefficient are necessary. The measurement of the optical parameters has been based on the assumption that light scattered from biological media is isotropically distributed over all angles. In fact, the optical behavior of real biological materials depends on the angular scattering of light due to the anisotropic nature of the materials. The purpose of the present work is to evaluate the optical properties (including color, opacity/translucence, scattering, and fluorescence) of zirconia dental ceramics and their control through modification of the chemical composition, phase composition, and surface microstructure.

Keywords—Optical properties, opacity/translucence, scattering, fluorescence, chemical composition, phase composition, surface microstructure.

I. INTRODUCTION

DENTAL restorations with the appearance of natural teeth require appropriate material selection, anatomical form, and surface texture as well as adequate translucence and color to create light reflection and absorption characteristics similar to those of natural teeth [1].

Apart from zirconia, dental ceramics such as lithium disilicate, feldspathic bodies, and glass-ceramics can have good aesthetic outcomes when bonded to non-discolored natural tooth structures due to their capability of transmitting light through the ceramic bulk [2]. In addition, such dental ceramics are color-stable and more wear-resistant than composite restorations [3]. However, inadequate mechanical performance limits their applications. Advanced zirconia-based dental ceramics can be used in low-load areas of the mouth with greater structural reliability thereby achieving

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longer restoration lifetimes [3] due to their high mechanical strength and fracture toughness [4], [5]. Zirconia was introduced to prosthetic dentistry in 1986 with the InCeram Zirconia system (Vita Zanhfabrik, Germany), which was handmade [6].

Pure zirconia at room temperature has a monoclinic crystal structure and transforms to the tetragonal phase above 1170 °C and a cubic phase above 2370 °C [4]. These phase transformations in pure zirconia are reversible but, in zirconia-stabilized systems, they may be irreversible. The tetragonal-to-monoclinic phase transformation upon cooling is accompanied by an increase in volume (3-5%), which, for densified components, results in extensive microcracking and compromised mechanical properties. Doping zirconia with various oxides can stabilize the tetragonal and cubic phases to room temperature [4], thus avoiding this phase transformation and its detrimental effects on the mechanical properties.

Three different types of zirconia materials have been developed for dental applications: Tetragonal ZrO_2 mechanically dispersed as a minor phase in an alumina matrix, forming an Al_2O_3-ZrO_2 composite known at zirconia-toughened alumina (ZTA); tetragonal ZrO_2 precipitated as a minor phase in a cubic matrix, known as partially stabilized zirconia (PSZ); and single-phase tetragonal ZrO_2, known as tetragonal zirconia polycrystal (TZP) [7]. InCeram Zirconia is the only dental ceramic toughened through mechanical dispersion (in contrast with precipitation). It is formed by slip casting a mixture of alumina with 33 mol% zirconia (zirconia stabilized with 12 mol% ceria CeO_2) [8]. PSZ has been utilized as a dental ceramic in which tetragonal ZrO_2 particles occur as a precipitated phase in a matrix of cubic stabilized zirconia [9]. Typically, 8-10 mol% magnesia MgO is used to partially stabilize the zirconia but the formation of a magnesium silicate phase (either enstatite $MgSiO_3$ or forsterite Mg_2SiO_4) during heat treatment can degrade the mechanical properties of the material [7]. For both dispersed and precipitated tetragonal zirconia, the stabilization of the tetragonal phase at room temperature is determined by both the type and amount of dopant as well as the zirconia particle morphology (e.g., size, shape, and distribution in the matrix phase) [9]. TZP typically is doped with 2-4 mol% yttria Y_2O_3 (and is referred to as Y-TZP) and consists of >98% metastable tetragonal phase of fine grain size (~0.2-0.5 μm) [7].

Computer assisted design (CAD) and computer assisted manufacturing (CAM) have been utilized in dentistry to obtain infrastructural and prosthetic abutment with the tooth or

implant. In these techniques, fully-sintered or partially-sintered blocks of monolithic zirconia are machined to the required shape, dimensions, and tolerances. In the case of partially-sintered blocks, implants/restorations are machined up to 30% larger than the final size in order to compensate for shrinkage during sintering [10].

Following preparation of a zirconia dental restoration using CAD/CAM and sintering, porcelain can be applied as a veneer and sintered onto the zirconia (Fig. 1). Porcelain veneering of the zirconia requires cooling at a sufficiently slow rate so as to minimise thermal gradients and internal stresses which, ultimately, reduces the incidence of fracture, chipping etc. of the veneered restoration [11]. However, there appear to be no long-term clinical studies to confirm the avoidance of fracture. The avoidance of cohesive failure of the veneering material arguably could be a reason to develop full-contour zirconia dental restorations (Fig. 2) [4], [12]. However, the use of full-contour zirconia in dental applications has challenges, such as translucence when used in the aesthetic zone, long-term clinical stability, and tribological behavior [4]. Recent developments focus on improving the optical properties of full-contour zirconia restorations without veneering material [13].
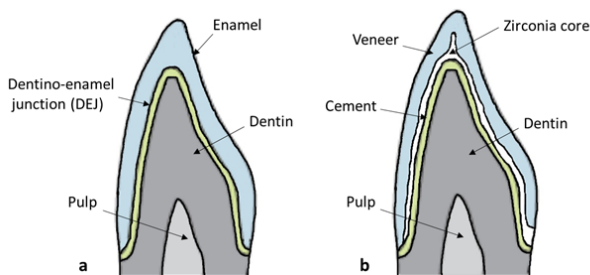

Fig. 1 (a) Schematic illustration of natural tooth structure (b) replaced by a zirconia core dental restoration
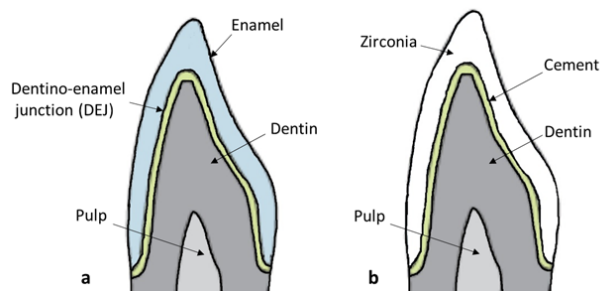

Fig. 2 (a) Schematic illustration of natural tooth structure (b) replaced by full-contour zirconia of monolithic zirconia

In the field of dental restorations, three ceramic materials have been introduced recently for full-contour zirconia restorations: Monolithic zirconia, zirconia-containing lithium silicate, and interpenetrating phase composites [4], which are discussed next. Since monolithic zirconia is the most important and widely-used of these three, it is the focal point of the present work, with less emphasis on lithium silicate and

interpenetrating phase composites.

II. MONOLITHIC ZIRCONIA

Monolithic zirconia generally refers to a dental restoration consisting of a single unit. While several of the zirconia materials mentioned are used, zirconia doped with 3 mol% (Y-TZP) is the most widely used zirconia material for dental applications [7] and hence is examined in detail. The term *monolithic zirconia* refers to Y-TZP unless otherwise noted.

III. ZIRCONIA-CONTAINING LITHIUM SILICATE CERAMICS

Lithium silicate glass-ceramics with additions of zirconia have been shown good optical and mechanical properties [4]. Two types of glassy matrices, lithium metasilicate and lithium disilicate, have been used, with zirconia acting as a nucleating agent [4]. Different amounts of zirconia (up to 20 wt%) in lithium metasilicate have been shown to give good thermomechanical and optical properties [14]. Fine-grained lithium silicate glass-ceramics, with both 4 wt% and 10 wt% zirconia also have been used as dental restorative materials [4], [15]. The Li_2O/SiO_2 with equal molar ratio of Li_2O to SiO_2 shows excellent mechanical and optical properties for dental applications [16]. Since zirconia has a higher molecular weight than stoichiometric lithium disilicate, the addition of zirconia increases the true density. As a result, the refractive index increases [17]. Lithium disilicate glass-ceramics, toughened with ZrO_2, also show decreases in the volumetric nucleation and crystal growth rates due to high critical cluster formation in the vicinity of glass transition temperature [16]. Although zirconia addition increases the refractive index of lithium disilicate, the effects on the other optical properties were not reported. However, it is likely that a decrease in crystallisation would result in the formation of smaller crystals and a smaller total volume of crystals. Both effects would be expected to decrease light scattering and improve translucence of the glass-ceramic.

IV. INTERPENETRATING PHASE COMPOSITES

Interpenetrating phase composite zirconia has been formed by liquid infiltration into a porous zirconia structure. The infiltrating liquid is either molten glass or a monomer that is subsequently polymerized to form a thermoset [4]. The use of zirconia was adopted from the earlier development of fully dense net-shape ceramics of alumina infiltrated with lanthanum-containing ceramics [4]. An example of such an interpenetrating phase composite is the 3M™ Paradigm™ MZ100 Block made for CEREC CAD/CAM systems. According to the 3M catalogue, "the block material contains 85 wt% ultrafine zirconia-silica ceramic particles that reinforce a highly crosslinked polymeric matrix. The polymer matrix consists of bisGMA (Bisphenol A diglycidyl ether dimethacrylate) and TEGDMA (tri [ethylene glycol] dimethacrylate). The ultrafine zirconia-silica filler particles are synthesized by a sol-gel process that results in a unique structure of nanocrystalline zirconia dispersed in amorphous silica" [18]. The primary objective of the development of

these interpenetrating phase composite materials is to facilitate clinical chairside CAD/CAM technology but the optical properties have not been reported and so require further examination [4].

V. MECHANICAL AND COMPOSITIONAL PROPERTIES OF MONOLITHIC ZIRCONIA

In general, the replacement of damaged tooth structures with dental restorations requires removal and preparation of the abutment tooth. The recommended prepared thickness for the abutment tooth depends on the mechanical properties of the restoration material. A thin wall thickness helps to reduce the need for invasive preparation, with correspondingly lower risk of pulp damage, which is particularly important for younger patients. Thus, the favourable mechanical properties of monolithic zirconia make this ceramic ideal for fabrication of thin restorations. The fracture resistance of monolithic zirconia with a thickness of only 1.0 mm is adequate to survive in the oral environment [13]. However, appropriate tooth preparation and choice of cement for monolithic zirconia crowns are critical to ensure adequate mechanical performance. Low-temperature degradation (LTD) of Y-TZP is another important issue (this is considered later). The rate of LTD is influenced by the fabrication processes for monolithic zirconia, such as sintering, secondary firing, and coloring procedures, which, collectively, determine the microstructural and mechanical properties of zirconia [4], [19], [20].

VI. DISCUSSION

General Discussion of Optical Properties

When light proceeds from one material to another, some of the light will be transmitted, some will be absorbed, and, at the boundary between the two materials, some of light will be reflected. Transparent materials are capable of transmitting light with insignificant absorption and reflection; translucent materials transmit a fraction of the light; opaque materials do not transmit the light.

Nonmetallic materials can be intrinsically either transparent (single-crystal) or opaque (polycrystalline). In general, valence-conduction band electron transitions and electronic polarization are two mechanisms that affect the light transmission characteristics of non-metallic materials [21]. Non-metallic materials having a relatively narrow band gap (less than ~1.8 eV) will absorb photons from all incident visible light (to excite electrons from the valence to the conduction band) and so will appear opaque. Non-metallic materials having a band gap in the range of ~1.8-3.1 eV will absorb a portion of the visible spectrum (depending on the band gap). Since the balance of light of these wavelengths (400-700 nm) is transmitted and reflected, color from transparent and opaque materials, respectively, is observed. Non-metallic materials having a band gap greater than ~3.1 eV will not absorb visible light and so will appear transparent and colorless. However, even with a band gap larger than ~3.1 eV, some light absorption can occur due to electronic polarization, giving a translucent appearance.

Refraction, reflection, scattering, and absorption (Fig. 3) of light must be considered. Transparent materials with band gaps greater than ~3.1 eV may appear translucent or opaque depending on the microstructure (e.g., grain size and thickness) [21]. Translucent materials allow light to be transmitted diffusely. This occurs when light is scattered to the extent that objects cannot be seen clearly through the material. The associated interaction with light derives from differences in refractive indices across different interfaces between grains, media, and pores. Further, light transmission is affected by other features, including the presence of different grains (secondary phases) and crystal orientation (anisotropic grains). Therefore, the amount of incident light absorbed, transmitted, reflected, refracted, and/or scattered will determine the translucence or opacity of materials.
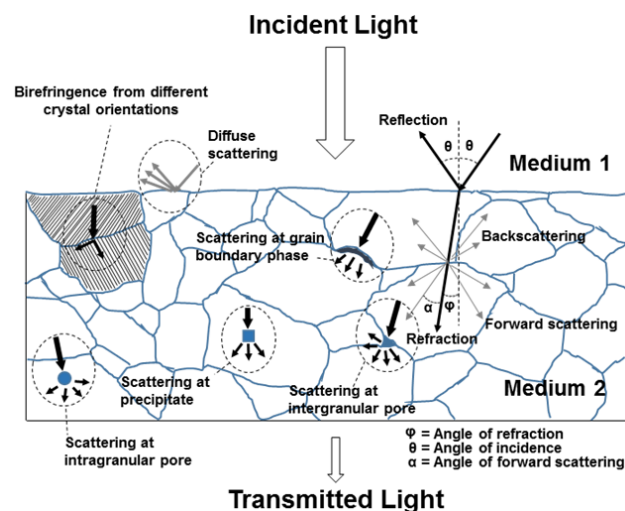

Fig. 3 Interaction light with materials and their microstructures

In general, the absorption coefficient (μ_a), the scattering coefficient (μ_s), and the scattering anisotropy factor (or phase function) (g) are three parameters that influence the light propagation through a material [22]. The scattering coefficient depends on: the wavelength of the incident light; the refractive index of the material; and the number, size, and shape of the grains of the microstructure that are causing scattering. When light is scattered by a particle, it is reflected by an angle α; α is 0° when photons continue in the original direction. The component of the new trajectory that is aligned in the original direction is proportional to the cosine of this scattering angle, $\cos \alpha$. The light scattered as a function of angle from a particle (scattering angular distribution) is characterized by the scattering anisotropy factor and defined by the mean value of the scattering angle [23].

The scattering anisotropy factor is a measure of the amount of light that is forward-scattered rather than back-scattered in a single scattering occurrence. A value of $g = -1$ indicates complete backscattering, while a value of $g = +1$ indicates complete forward-scattering; in the case of isotropic media (viz., monolithic amorphous materials and single crystals), $g = 0$. The light distribution becomes more uniform as the number

of scattering events increases.

When light travels through materials, both absorption (μ_a) and scattering (μ_s) coefficients must be considered; the sum of these two coefficients gives the transport coefficient ($\mu_{transport}$):

$$\mu_{transport} = \mu_a + \mu_s \tag{1}$$

Therefore, for calculation of the light transmission based on the transport coefficient, the absorption coefficient and scattering coefficient using the mean value of the scattering angle are required [23]. These data also provide information about the penetration depth since this (*viz.*, the mean free path) and the transport coefficient are related.

Behavior of Light in Natural Dental Tissues

Biological media usually are heterogeneous and this can cause significant transmission, reflection, and scattering [23]. Biological tissues are not comprised of discrete scattering and absorption centres; rather they exhibit volumetric scattering or absorption [22] according to:

$$V = \perp^x \rho \tag{2}$$

where V is volumetric scattering or absorption, $\perp$ is the cross sectional area of the scattered or absorbed light, and ρ is the true density of the absorbing or scattering phase. When light enters a natural tooth, it can be transmitted through the tooth, specularly reflected from the outer surface of the tooth, diffusely reflected from the buccal surface of the tooth, or absorbed/scattered in the dental tissues [24]. Reflection and absorption of the light are wavelength-dependent, so they determine the color of the tooth and are influenced by enamel thickness, shape, surface texture, the presence of interfaces between different materials, and the nature of the light source [24]. A greater thickness of enamel is present in proximal and incisal teeth than cervical. Therefore, natural teeth appear more translucent in the incisal area [25].

When light passes through the enamel and reaches the dentine, it can be reflected back to the enamel. The apparent color of the tooth thus is affected by the color of the dentine. In addition, enamel is highly mineralized tissue. The hydroxyapatite crystals in the enamel can scatter the blue wavelengths of light selectively while allowing longer wavelengths to be transmitted [26]. This selective scattering of shorter wavelengths gives the enamel a bluish-white color while longer wavelengths transmitted by the enamel can be reflected back by dentine and so produce an orange glaze (known as *counter-opalescence*) [27].

Dentine exhibits back-scattering of incident light due to the tubular structures that traverse the region from the pulp to the enamel [23]. In contrast, enamel shows forward-scattering.

Dentine is three times more fluorescent than enamel due to the larger amount of ultraviolet (UV) photosensitive organic pigment it contains [28]. When dentine is exposed to UV light, this pigment emits light at a range of wavelengths, from violet to intense blue light.

Behavior of Light in Zirconia Ceramics

The increasing expectation of patients for dental restorations to provide an aesthetic match with natural teeth creates a demand for more lifelike materials, mainly ceramic materials, for dental restorations. However, there is no single dental ceramic that can exhibit the complex behavior of light in natural dental tissue and simultaneously display the characteristics of opacity and translucence of natural dental tissue [24]. Furthermore, a lack of fluorescence in zirconia dental ceramics diminishes the natural appearance, which is accentuated by zirconia's propensity to change from white to grey under low-light conditions. In contrast, natural teeth remain essentially unchanged under these conditions [29].

Similar to natural dentine, zirconia back-scatters incident light. Thus, zirconia can give a similar appearance to dentine but less so for enamel. However, in dental restorations, zirconia is used more often to replace enamel.

The band gap of undoped tetragonal zirconia is 3.0-4.5 eV (413-275 nm) and this increases to 5.2-6.0 eV (238-206 nm) when doped with 3 mol% yttria [30]. Thus, Y-TZP is not expected to absorb light significantly at wavelengths greater than 295 nm and so should be transparent to visible light. Hence, instead refraction, reflection and scattering of light in zirconia dental ceramics are the most important factors. Diffusion considerations can be applied to zirconia dental ceramics since light particles with energy $h\upsilon$ (h = Planck's constant; υ = frequency) and c (speed of light) are scattered or absorbed by zirconia and reflected at boundaries between different grains and pores of different refractive indices (laws of Fresnel) [31]. Since light not scattered in the forward direction is indistinguishable from unscattered light, a reduced scattering coefficient μ'_s is applied. The μ'_s of zirconia has been determined to be considerably higher than its μ_a although the trends as a function of wavelength are similar [22]. Therefore, the higher value of μ'_s will impact on the translucence (the inverse of scattering) more than the μ_a and so it is the focus of consideration [22]. Since the angular scattering distribution of zirconia is close to zero, then absorption dominates translucence. Translucence is the attenuation of light by a material in terms of the ratio of the intensity of the transmitted light relative to the intensity of incident light [21]. As shown in Fig. 4, in the visible light range (400-700 nm), different light sources exhibit different spectra [32]. These data have been used to identify the maximal intensities at different wavelengths (there are two with fluorescence light) over the range 400-700 nm. Since translucence also depends on the intensity of the incident light, then these two parameters were combined. The range of wavelengths considered ranged from ~520 nm (minimal measured μ_s; maximal translucence) to ~630 nm (maximal measured μ_s; minimal translucence), which encompasses the maxima for LED and fluorescent lights and high ranges for daylight and incandescent lights. A simplified comparison of the scattering data is done as follows:

1) Normalisation of the μ_s data [22] to 100%.
2) Identification of the maximal μ_s.
3) Identification of the μ_s values at the maximal wavelengths.

4) Determination of the percentage intensity at the wavelength of maximal intensity [32].
5) Multiplication of 3) by 4).
6) Subtraction of 5) from 2).

The data for 4) and 6) are shown in the bars in Fig. 4. These data show that, in terms of translucence, the best simulation of daylight is provided by LED light. Although the data for fluorescent light are similar, they derive from two discrete wavelengths while those for LED light and daylight are spread more consistently across the range of wavelengths of concern. This conclusion indicates that LED lighting should yield the best results for shade matching of zirconia restorations, laboratory and clinic environments, and internal ambient light conditions.
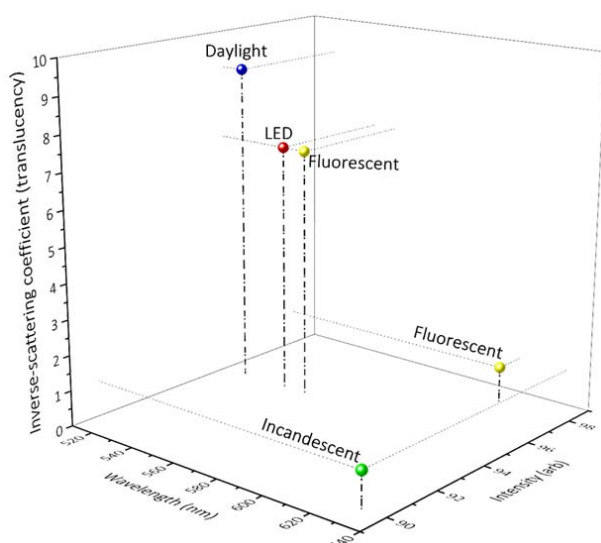

Fig. 4 Comparison of maximal intensities [32], and inverse-scattering values for corresponding wavelength(s) [22] of maximal intensity of each light source

Both intrinsic properties of a material and extrinsic parameters will affect significantly the color and appearance of all-ceramic dental restorations [33]. Therefore, in order to achieve the desired optical properties for dental applications, these intrinsic and extrinsic characteristics and their effects on the optical properties of zirconia must be considered and controlled.

Intrinsic Characteristics of Zirconia and Their Effects on Optical Properties

Higher amounts of light transmission generally are exhibited by homogeneous and isotropic (including polycrystalline cubic) materials. Zirconia ceramics are polycrystalline and, like polycrystalline ceramics in general, light transmission through them depends to a large degree on the microstructure. Several features, such as interfaces between different phases, birefringence, pores and grains of sizes similar to the wavelengths of visible light, and rough surface finish, can reduce the translucence of zirconia [34], [35]. Therefore, controlling the microstructure is important to achieve zirconia dental ceramics with the appearance of natural teeth.

Pores in ceramics can have a significant effect on the optical properties. In particular, when they are of size similar to the wavelengths of visible light (400-700 nm), they are the main cause of light scattering [36]. Therefore, elimination of submicron pores is necessary to decrease the opacity of dental ceramics. Intergranular and intragranular pores are two different types of pores that have different optical characteristics. The intergranularity locates the pore between typically two or three crystalline grains of different orientations in a narrow volume (grain boundary), which effectively can be considered to be an amorphous phase. Intragranular pores represent discrete interfaces between two effectively isotropic phases. Decreasing the grain size tends to reduce the pore size commensurately [37]. Further, the removal of gas entrapped within closed (intragranular) pores, which hinders pore elimination, is facilitated by finer grain sizes. Low-temperature presintering of zirconia generally produces microstructures of small intergranular pores surrounded by fine grains while, for high-temperature presintering, grain growth takes place and intergranular pores can transform to intragranular pores, which are much more difficult to eliminate. Thus, using a fine grain size and applying low-temperature presintering is expected to result in greater probability of pore elimination [37] and a significant reduction in light scattering. Furthermore, hot isostatic pressing of low-temperature presintered ceramics can result in almost complete pore elimination [38].

The majority of polycrystalline zirconia materials used in dental applications are processed in this way and they are 99.9% dense [36]. Also, most zirconia dental ceramics are in nanocrystalline form and of grain size <50 nm, which suggests that pores larger than 50 nm are unlikely. Since this mean free path is significantly less than the wavelength range of visible light, their interaction can be expected to be minimal. Further, most dental ceramics are made from 3Y-TZP, in which the yttrium stabilizer acts as a pore scavenger, resulting in reduction of intragranular pore formation [37]. Consequently, it can be concluded that porosity has only a minor influence, if any, on the optical behavior of modern nanocrystalline zirconia dental ceramics.

Crystallites of nanocrystalline zirconia powders can be used to yield smaller grain sizes than powders consisting of submicron polycrystals [39]. Different techniques to synthesise nanoscale zirconia have been used, including co-precipitation [40], sol-gel [41], hydrothermal treatment [42], combustion synthesis [43], and mechanochemical processing [44]. However, grain coarsening is inevitable during pressureless sintering, hot pressing, or hot isostatic pressing [34] and this results in larger grain sizes and consequently reduced mechanical and optical properties [45]. Although large grain sizes result in less scattering at grain boundaries due to their smaller total area, greater residual porosity results and this has been shown to have a greater effect on light scattering than grain boundaries [46]. Therefore, reduction of the residual porosity in dental ceramics is critical. In addition

to the preceding densification methods, spark plasma sintering (SPS) has been developed to obtain fully dense nanocrystalline ceramics [47]. SPS can produce ceramics with pores of only 10-20 nm in diameter, which are very much less than the wavelengths of light. Regardless, significant light absorption and scattering still can occur at the shorter light wavelengths [46]. Alaniz et al. [36] found that the optical transmission and reflectance of nanocrystalline zirconia (grain size ~55 nm) heated by SPS at 1200 °C under vacuum progressively decreased with sintering time and this correlated with increased absorption. This was attributed to an increase in the concentration of oxygen lattice vacancies (occurring as a result of the high-temperature reducing conditions typical of SPS) which give greater optical absorption (particularly at ~450–500 nm) [36], [46]. Subsequent annealing in air at a moderate temperature (~750 °C) tended to increase transparency and decrease absorption despite the fact that the porosity and grain size would not be expected to change with heating at this temperature owing to the low cation mobility [36] – this was attributed to a consumption of oxygen vacancies owing to the availability of atmospheric oxygen. These observations highlight the critical importance of oxygen vacancy concentration to the optical properties.

Microwave sintering is an alternative approach to the densification of nanocrystalline zirconia. The electromagnetic waves polarize interatomic bonds in ZrO_2 and movement of the dipolar species generates heat that is conducted through the material. Zirconia couples poorly with microwaves below 400 °C [48], so a silicon carbide (SiC) susceptor for hybrid heating can assist in initial heating [49]. Compared with conventional heating, microwave sintering has the advantages of rapid and uniform heating which can result in significantly shortened heat treatment times thus decreasing the extent of grain growth which, ultimately, produces ceramics having higher bulk densities and significantly finer and more uniform grain sizes [49]-[51].

In addition to controlling the microstructure through processing, dopants can be used to modify the optical properties. For example, the addition of 0.2 mol% lanthana (La_2O_3) to 0.1 wt% Al_2O_3-doped Y-TZP significantly improves translucence [51]. The La_2O_3 dopant completely dissolves in the zirconia, which results in a finer microstructure free of precipitation by secondary phases [52].

Research on controlling the color of zirconia to match natural tooth color has focused mainly on the effects of Fe-doping of zirconia nanopowders on the microstructure and mechanical properties [53], [54]. Other work has examined the mechanochemical processing of Pr-doped 3Y-TZP nanopowders [55]. The mechanochemical processing of Pr-doped 3Y-TZP nanopowders using $ZrOCl_2.8H_2O$, $YCl_3.6H_2O$, and $PrCl_3.7H_2O$ as raw materials is promising for dental restorations because the results indicate biocompatibility coupled with a good aesthetic outcome [55].

In general, point defects, such as oxygen vacancies, can be generated thermally or by dopants [56]. Zirconia must be stabilized by the addition of dopants in order to avoid the tetragonal-to-monoclinic phase transformation. Since zirconium ions are tetravalent, if the stabilizing dopants are divalent or trivalent (e.g., Y^{3+}, Fe^{+2}, Fe^{+3}, Ni^{+2}, Cr^{+3}), they must be charge-compensated by the introduction of positively-charged defects, such as oxygen vacancies [57]. Thus, the valence, concentration, ionic radius of the dopant, and the processing temperature will influence the defect distribution and defect stability [56] and thus the optical properties. In the case of Y^{3+} for stabilization, since Zr^{4+} is smaller than Y^{3+}, oxygen vacancies are formed and, when present at high levels, can form defect clusters [58], which are detrimental to the optical performance.

Y-TZP monolithic zirconia compositions for dental restorations intrinsically contain hafnia HfO_2, typically at levels ≤5 mol%), yttrium oxide (4.5 < Y_2O_3 ≤ 6 mol%), and <1 mol% other oxides, particularly aluminium oxide (Al_2O_3). The presence of Al_2O_3 enhances the densification rate of zirconia but it reduces the transmission of visible light due to segregation of Al_2O_3 on the ZrO_2 grain boundaries [59].

Extrinsic Characteristics of Zirconia and Their Effects on Optical Properties

Cementing

In addition to the factors mentioned above, the final appearance of ceramic restorations is affected by the cement composition. Clinicians frequently are faced with the challenge of selecting an appropriate shade of luting agent to adjust the final color of the restoration [60]. Polymer resin-based cements provide higher compressive strengths than zinc phosphate cements. In addition, adhesive resin-bonding is necessary to ensure better retention and marginal adaptation [61]. However, owing to the inability to satisfactorily etch zirconia, adequate micromechanical adhesion to polymer resin-based cement cannot be obtained. Zirconia`s inertness and glass-free composition limit adhesive luting potential [62]. Therefore, for zirconia dental restorations, dual-polymerizing cements are used commonly. It polymerizes the cements with use of both chemical and light [61].

While not ideal in terms of mechanical performance, polymer resin-based cements sometimes are used with zirconia ceramics to fulfil the marginal integrity. In this case, the surface of the zirconia must be modified in order to obtain durable bond strength. It has been claimed that an abrasive surface treatment and/or silica-coating treatment with the use of a primer can produce adequate bond strength [20]. However, this claim requires clinical evidence and the effect of such surface modifications on the optical properties of zirconia have not been reported.

Achieving an adequate degree of monomer conversion of light-curing cements depends on light irradiance through the zirconia material, which depends on the thickness and optical properties. Therefore, the development of improved optical properties (e.g., more translucent zirconia) for dental applications not only enhances the aesthetic quality but also improves the photopolymerization of the composite cement since zirconia's opacity impairs adequate polymerization of light-cured cement [63]. The presence of Al_2O_3 in zirconia ceramics also has been shown to increase significantly the

degree of monomer conversion by increasing the curing light transmission [64]. With dual-polymerizing cements, chemical polymerization can compensate poor light irradiance partially through the zirconia. However, very low initial light irradiance cannot be compensated adequately by chemical polymerization and early failure of retained zirconia restorations can occur [64]. Optimization of the light-polymerization protocol and light source also can be used to improve photopolymerization [64].

Although self-cured cements are alternative options, dual-polymerizing cements, including the light-cured component, are significantly more effective than self-cured cements in terms of retention and marginal adaption [65], [66].

Thickness

In addition to translucence being dependent on composition, the amount of light transmitted also is dependent on material thickness [67]. According to the Beer-Lambert law, the amount of transmitted light $F(x)$ is given by:

$$F(x) = a \cdot \exp(-bx) \qquad (3)$$

where a is the initial irradiance, b is a material constant, and x is the thickness (*viz.*, optical path length) [67]. The rate of change of translucence with thickness can be obtained from the derivative of (3), which indicates that translucence depends exponentially on x:

$$F'(x) = -ab \cdot \exp(-bx) \qquad (4)$$

where the material constant b is the absorption coefficient and equal to $4\pi k/\lambda$, where k is the index of absorption and λ is the light wavelength. Therefore, the fraction of transmitted light is a function of both the absorption coefficient of the material and the material thickness, which highlights the importance of the thickness of dental prostheses [68].

Low Temperature Degradation (LTD)

While zirconia has sufficient mechanical properties for dental restorations, one limitation is that it suffers from LTD. This degradation occurs due to exposure of zirconia to saliva/water and cyclic loading which causes premature tetragonal-to-monoclinic phase transformation which results in a reduction of the modulus of elasticity, flexural strength, and fracture toughness [20]. Three hypotheses have been proposed to explain LTD: (1) diffusion of hydroxide ions from water (OH^-) into the crystal lattice via oxygen vacancies, resulting in a change in the crystal structure [69]; (2) reaction of water with Y_2O_3 to form clusters rich in $Y(OH)_3$ [70]; and (3) water vapour attack of Zr-O bonds, which induces movement of OH^- and thus generates lattice defects that act as nucleation sites for the phase transformation [71].

Both a finer grain size and higher Y_2O_3 concentration have been suggested to retard the LTD [72]. A small grain size of Y-TZP effectively hinders the tetragonal-to-monoclinic phase transformation, hence slowing the rate of LTD. Similarly, Y^{3+} ions in the grain interior also stabilize the tetragonal phase and slow the LTD. However, hindering the phase transformation also impedes the toughening mechanism and reduces its mechanical benefits.

The Y_2O_3 concentration has a significant influence on the bulk density and average grain size of zirconia. Increasing the Y_2O_3 concentration (above 3 mol%) increases the amount of cubic phase present. This decreases the mobility of the grain boundaries [73], thus affecting densification and the distribution of the tetragonal phase [74], thus ultimately degrading the mechanical properties. Further, higher concentrations of Y_2O_3 result in higher charge-compensating oxygen vacancy concentrations, which increase the LTD rate [75].

The Y^{3+} ion distribution usually is homogenous in raw Y-TZP powders used for synthesis [76], [77]. However, processing at temperatures above the tetragonal-to-cubic phase transformation temperature for the Y_2O_3-ZrO_2 system (~1300 °C) can redistribute the Y^{3+} ions, resulting in the phase separation into discrete tetragonal (~2 mol% Y_2O_3) and cubic (6-8 mol%) phases. This decreases the microstructural homogeneity of the material and degrades the mechanical properties.

For TZP ceramics in general, the LTD rate is influenced by the amount and type of stabilising oxide, grain size, and bulk density [78]. Obtaining fully densified Y-TZP powder is challenging owing to the requirement of pressureless sintering at temperature below 1300 °C. In addition, it requires sufficient Y_2O_3 for tetragonal ZrO_2 stabilization and sufficiently small grain size.

Y-TZP containing Al_2O_3 can be sintered at temperatures less than 1300 °C in air and so alumina additions have been used to overcome the LTD of Y-TZP ceramics [79]. Nanocrystalline 3Y-TZP doped with Al^{3+} and Ge^{4+} ions formed by pressureless sintering at temperatures below the tetragonal-to-cubic transformation temperature have shown significantly accelerated densification. This highlights the importance of sintering to control the zirconia microstructure in order to improve the LTD resistance [72]. However, Y-TZP containing Al_2O_3 has grain size distributions of 400-600 nm, which are similar to the visible light range. This results in significant light scattering and consequent low translucence of zirconia-alumina composite ceramics [80].

VII. SUMMARY

In the present work, issues relevant to the use of zirconia ceramics for aesthetic dental restorations and improvement in their optical properties have been discussed. The intrinsic and extrinsic properties of ZrO_2 and their effects on the optical properties are understood at a basic level but they require further elucidation, especially when considered in terms of clinical outcomes. Intrinsic characteristics; such as chemical composition, defect structure (oxygen vacancies), phase composition (secondary phases, phase distribution), closed porosity, and grain size; as well as extrinsic properties; such as underlying tooth structure, surface topography, material thickness, type and thickness of cement layer, and light source (natural, curing; artificial), are of considerable significance and so require further study in order to understand their effects

on the refractive indices, transmission, absorption, reflection, scattering, and their effects on the color and translucence of zirconia dental restorations.

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