



치의과학박사 학위논문

# Effect of phase fraction and grain size on translucency of 3Y-TZP dental zirconia

3Y-TZP 지르코니아 결정상 분율과 입자 크기가 투광도에 미치는 영향

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조 준 호

# Effect of phase fraction and grain size on translucency of 3Y-TZP dental zirconia

지도교수 한 중 석

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### ABSTRCT

# Effect of phase fraction and grain size on translucency of 3Y-TZP dental zirconia

Jun-Ho Cho, D.D.S., M.S.D.

Program in Prosthodontics, Department of Dental Science,

Graduate School, Seoul National University

(Directed by Professor Jung-Suk Han, D.D.S., M.S., Ph.D.)

**Purpose.** This in vitro study aimed to evaluate the effect of phase fraction of zirconia polymorphs and grain size on the translucency of 3Y-TZP.

**Material and methods.** Disk-shaped specimens were fabricated with alumina-free 3-mol% yttria-stabilized zirconia polycrystal powders. Based on the final sintering temperature and holding time, 8 groups (n = 10) were established: 1500°C-2h, 1550°C-2h, 1570°C-2h, 1570°C-5h, 1570°C-10h, 1570°C-15h, 1570°C-20h, and 1600°C-2h groups. Sintered specimens were ground and polished on both sides into the final dimension with 14.0-mm diameter and 1.0-mm thickness. Light transmittance, biaxial flexural

strength, and density were measured. The mean grain size was calculated with a scanning electron microscope. The crystalline phases were investigated with X-ray diffraction analysis and Rietveld refinements. Oneway analysis of variance, Welch analysis of variance, and a post-hoc pairwise comparison were used for analysis ( $\alpha = .05$ ).

**Results.** Translucency and mean grain size significantly increased (P < .05), tetragonal (t) phase fraction decreased, and cubic (c) and tetragonal doubleprime (t'') phase fractions increased as the sintering temperature increased. As the holding time increased, translucency was not significantly different among the groups, except 1570°C-2h group (P < .05), mean grain size significantly increased (P < .05), t-phase fraction decreased, and t"-phase fraction increased. c-phase fraction increased with holding time from 2- to 15-hour and then slightly decreased with further holding to 20-hour. Flexural strength was not significantly different among the groups. All groups showed density with more than 99% of the theoretical value. As the sintering temperature and holding time increased, the tetragonality of the tetragonal phase increased, and the yttria (Y<sub>2</sub>O<sub>3</sub>) content of the tetragonal phase decreased. Yttria content of the cubic phase increased as the sintering temperature increased and maintained from 5- to 20-hour holding time. By comparing with as-sintered specimens, t- and c-phase fractions decreased, and t''- and rhombohedral (r) phase fractions increased after grinding and polishing.

Conclusions. Translucency was affected by all contributing factors,

including crystalline phase fractions, mean grain size, tetragonality of the tetragonal phase, and density. Increased *c*- or *t*"-phase fractions and *t*-phase fraction above critical level by suppressing other undesired phases would improve the translucency without compromising the strength and toughness of 3Y-TZP.

**Keywords:** 3Y-TZP; Translucency; Phase fraction; Zirconia polymorphs;

Grain size; Flexural strength

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### ABSTRACT IN KOREAN

# I. INTRODUCTION

A 3-mol% yttria-stabilized tetragonal zirconia polycrystal (3Y-TZP), which features high strength and toughness, tooth color aesthetic, more conservative tooth preparation, biocompatibility, minimized wear on an antagonist, and low cost, has become widely used as a restoration material in dental clinics (Ghodsi and Jafarian, 2018, Pekkan et al, 2020, Kontonasaki et al, 2019, Zhang, 2014, Albashaireh et al, 2010, Stawarczyk et al, 2013, Nordahl et al, 2015). Although 3Y-TZP is fairly aesthetic, opacity or low translucency is the main drawback that makes zirconia restorations look different from natural teeth or dental porcelain (Zhang, 2014, Tong et al, 2016, Sulaiman et al, 2015, Vagkopoulou et al, 2009, Sravanthi et al, 2015). The optical properties, mechanical integrity (strength and toughness), and long-term reliability (resistance for low-temperature degradation) of 3Y-TZP are complexly related to the microstructures, including phase fraction and grain size, pores, impurities, defects, flaws, and surface conditions, and are affected by sintering parameters, yttria  $(Y_2O_3)$ content, and powder size (Zhang, 2014, Klimke et al, 2011, Yamashita and Tsukuma, 2011, Zhang et al, 2012, Anselmi-Tamburini et al, 2007, Pekkan et al, 2020). Since the partially stabilized cubic zirconia with higher translucency shows significantly lower strength than the 3Y-TZP and is restricted for use in the posterior area, 3Y-TZP with improved translucency has the potential to have advantages in both mechanical and optical

properties (Klimke et al, 2011, Zhang, 2014, Casolco et al, 2008, Trunec and Chlup, 2009).



**Figure 1.** Schematic representation of polymorphisms of zirconia. A, Lengths a, b, and c of unit cell edges and angles  $\alpha$ ,  $\beta$ , and  $\gamma$  between edges. B, Unit cell of crystalline polymorphic phases: monoclinic (*m*), tetragonal (*t*), tetragonal double-prime (*t*"), cubic (*c*), and rhombohedral (*r*).

Pure zirconia presents in three crystallographic forms depending on the temperatures: monoclinic (*m*) from room temperature to 1170°C, tetragonal (*t*) between 1170°C and 2370°C, and cubic (*c*) above 2370°C (Fig. 1) (Subbarao, 1981, Franco-Tabares et al, 2021). Partial stabilization of tetragonal zirconia, which has metastability, can be achieved by adding 2–5 mol%  $Y_2O_3$  stabilizing oxides to pure zirconia (Garvie et al, 1975, Garvie and Nicholson, 1972). High strength and toughness of tetragonal zirconia to monoclinic phase (*t* to *m*), which accompanies volume expansion of approximately 4.5% (Heuer et al, 1986). It was reported that tetragonal double-prime (*t*") and rhombohedral (*r*) phases also exist (Fig. 1). *t*"-phase has a unit cell, similar to the cubic unit cell, with the oxygen vacancies

displaced along the c-axis, and it is known to be originated from *c*-phase by an ordering mechanism of an anionic sublattice, thus has a tetragonality close to 1 and small birefringence (Cairney et al, 2007, Yashima et al, 1993, Belli et al, 2021, Lughi and Clarke, 2005). r-phase was known to be observed when the low-temperature degradation happens or surface grinding was conducted (Kosmač and Kocjan, 2012, Kim et al, 1995). c-phase is isotropic, but other phases (t, m, t'', and r-phases) have anisotropic refractive indices in different crystallographic directions. The birefringence of m-ZrO<sub>2</sub> is known to be 0.070, and t-ZrO<sub>2</sub> has no reliable data (Klimke et al, 2011). By the phase diagram of Scott, 3Y-TZP sintered at typical sintering temperatures contains both tetragonal and cubic phases at room temperature (Scott, 1975). The presence of cubic phase was experimentally proved, and a significant amount of cubic phase was observed with a sintering temperature above 1550°C (Chevalier, 2004, Ruiz and Readey, 1996, Matsui et al, 2003). Higher sintering temperatures would migrate yttria to the grain boundaries so that cubic phase at grain boundaries or high-yttria tetragonal phase near the grain boundaries are formed, and low-yttria tetragonal phase appears in the grain interior (Stawarczyk et al, 2013, Scott, 1975, Denry and Kelly, 2008, Chevalier, 2004, Matsui et al, 2022). On the other hand, some previous studies reported that the cubic phase would not exist at room temperature for 3Y-TZP, even with no evidence for reputing the presence of cubic phase from Rietveld refinement (Belli et al, 2021, Lakiza et al, 2006). Thus, microstructural features and phase equilibrium should be appreciated to assess the effect of grain size on the translucency of 3Y-TZP.

The grain size of polycrystalline zirconia plays an important role in translucency because grains interact with light and optical phenomenon takes place (Vichi et al, 2014, Vichi et al, 2016, Hallmann et al, 2012). To obtain translucency similar to that of dental porcelain, it was reported that the grain size of 3Y-TZP should be smaller than 100 nm (Zhang, 2014). Currently used commercial dental zirconia has a tetragonal grain size of 0.2 to 0.8 µm, and it is still challenging to fabricate zirconia with grain size smaller than 100 nm with no porosity and defects, which is the source of light scattering (Zhang, 2014). A zirconia with grain size in the range of 0.1 to 1.0  $\mu$ m, which overlaps to the wavelength of visible light (range of 400 to 700 nm), is largely opaque due to the scattering, compared to that of grain sizes under 0.1 µm or above 1.0 µm (Zhang, 2014, Pekkan et al, 2020, Alaniz et al, 2009, Subaşi et al, 2018). In addition, it was reported that 3Y-TZP becomes less stable and spontaneous phase transformation from t to moccurs above a critical grain size, and 3Y-TZP with a grain size below a certain grain size (~  $0.2 \mu m$ ) becomes too stable that it cannot undergo the transformation from t to m, resulting reduced fracture toughness (Heuer et al, 1982, Cottom and Mayo, 1996, Denry and Kelly, 2008). For improved translucency, it is necessary to elucidate grain size dependence of the translucency of 3Y-TZP, whose grain sizes range from 0.1 to 1.0 µm; however, it is hard to explain with classical physics to interpret the change in optical properties raised by different grain sizes because of the unique

light scattering phenomenon of zirconia polycrystalline structure depending on the grain size (Pekkan et al, 2020). There have been several attempts to relate the grain size of 3Y-TZP to translucency. Rayleigh-Gans-Debye (RGD) scattering model works well for alumina but not for 3Y-TZP because of its large birefringence (Zhang, 2014, Klimke et al, 2011, Apetz and van Bruggen, 2003, Krell et al, 2009, Pekkan et al, 2020). Rayleigh scattering model can explain only 3Y-TZP, whose size is smaller than 80 nm (Pekkan et al, 2020, Zhang, 2014). For the grain size greater than 80 nm, the Mie scattering model, which is independent of the grain size, should be used; however, there are some difficulties in adapting the model (Zhang, 2014, Klimke et al, 2011). Thus, the correlation between grain size and translucency has not been fully understood yet for dental zirconia. There are some aspects of the effect of grain size on translucency. The translucency increases as grain size increases since the grain boundary area, a source of light scattering, decreases as grain size increases (Pekkan et al, 2020, Denry and Kelly, 2014, Kilinc and Sanal, 2021, Ebeid et al, 2014, Jiang et al, 2011, Sen et al, 2018, Stawarczyk et al, 2013, Coble, 1962). In contrast, it has been reported that the increase in grain size results in a decrease in the translucency due to the birefringence of tetragonal zirconia crystal or large scattering occurs when the grain size is similar to the visible light wavelength (Kontonasaki et al, 2019, Kim et al, 2013, Vichi et al, 2016, Kim and Kim, 2017, Tuncel et al, 2016). Because the tetragonal phase has an anisotropic refractive index in different crystallographic directions and large birefringence, whereas the cubic phase is isotropic and has a large grain size with fewer grain boundaries, a large portion of the cubic phase decreases grain boundary scattering, thus, is helpful in translucency (Pekkan et al, 2020, Zhang et al, 2015, Cardoso et al, 2020). A 3Y-TZP with large grain size would be accompanied by trapped pores inside the grains or enhanced crack formation leading to a decreased translucency or it would have an increased cubic phase fraction to contribute to a high translucency (Tekeli and Erdogan, 2002, Tuncel et al, 2016, Stawarczyk et al, 2013, Chevalier et al, 1999, Kim et al, 2013, Zhang et al, 2020, Lange, 1986). Increase in the sintering temperature and time leads to a larger grain size of zirconia (Chevalier, 2004, Denry and Kelly, 2008). At the same time, as the sintering temperature increases, the sintered body becomes more compact to decrease in porosity, defects, and flaws (Jiang et al, 2011, Vichi et al, 2016). Translucency increases as sintering temperature and time increase as a result of balance among many contributing factors, such as increased grain size, increased density, and increased cubic phase fraction (Ebeid et al, 2014, Pekkan et al, 2020, Stawarczyk et al, 2013, Jiang et al, 2011, Gómez et al, 2016).

Therefore, the purpose of this in vitro study was to evaluate the effect of phase fraction and grain size on the translucency of 3Y-TZP to provide a guideline for the optimum clinical application of dental zirconia. The research hypothesis was that the change in crystalline phase fraction and grain size would affect the translucency of 3Y-TZP.

# **II. MATERIAL AND METHODS**

#### **II. 1. Specimen fabrication**

Alumina-free 3Y-TZP powders ( $D_{50} = 0.56 \mu m$ ) (HSY-3F-J-NA, Daiichi Kigenso Kagaku Kogyo Co., LTD, Osaka, Japan) were used to fabricate specimens with improved translucency, and decreased low-temperature degradation resistance due to lack of alumina would be compensated by a higher *c*-phase fraction (Zhang, 2014, Zhang et al, 2012). With the cold isostatic pressing (CIP) technique, the powders were pressed uniaxially at 125 MPa in a steel die, then pressed isostatically at 186 MPa to produce disk-shaped green stage specimens with a diameter of 20 mm and thickness of 1.5 mm. The shaped specimens were sintered with the following sintering conditions: heating room temperature to the final sintering temperatures (1500°C, 1550°C, 1570°C, and 1600°C) with a heating rate of 100°C/hour, holding at final sintering temperatures for 2 hours, then cooled to room temperature in the furnace. For a sintering temperature of 1570°C, which showed the high translucency and flexural strength from preliminary experiments with groups sintered for 2 hours at different sintering temperatures, additional specimens were fabricated with holding times of 5, 10, 15, and 20 hours. After sintering, the specimens were ground and then polished with 6-, 3-, and 1-µm diamond particles in sequence (SPL-15 Grind X, Okamoto, Tokyo, Japan) for one side, and then the procedures were conducted on the opposite side, to the final dimension with a diameter of 14.0 mm and thickness of 1.0 mm. Based on the final sintering temperature and holding time, 8 groups (n = 10) were established: 1500°C-2h, 1550°C-2h, 1570°C-5h, 1570°C-10h, 1570°C-15h, 1570°C-20h, and 1600°C-2h groups.

#### II. 2. Translucency analysis

For translucency analysis, luminous transmittance was measured in accordance with ISO 13468-1:1966 with a haze meter (NDH-2000N, Nippon Denshoku, Tokyo, Japan), set up with a temperature of  $23^{\circ}C \pm 2^{\circ}C$  and relative humidity of 50%  $\pm$  5% (ISO, 1966, Hong et al, 2020). Total luminous transmittance (T) was calculated using the following equation:

$$T = \frac{L_{\text{specimen}}}{L_{\text{incident}}} \times 100$$

where  $L_{specimen}$  is the total light transmitted by the specimen, and  $L_{incident}$  is the measured quantity of incident light. Measurement was conducted three times for each specimen, and the average values were recorded.

#### II. 3. X-ray diffraction (XRD) analysis

Crystal phase fractions of zirconia polymorphs were investigated by XRD analysis with a diffractometer (Empyrean, Malvern Panalytical BV, Brighton, UK). Cu radiation (40 kV and 30 mA) and the range of the measured diffraction angle (2 $\theta$ ) was set to 20 to 90 degrees with a step size

of 0.0263 degrees. The polycrystalline phase fraction and lattice parameters were determined from the Rietveld refinements with a software program (HighScore Plus, Malvern Panalytical BV, Brighton, UK) (Rietveld, 1969). t-, t''-, m-, r-, and c-phases were included for analysis with the Rietveld refinements. The yttria content inside the tetragonal phase was estimated from the tetragonality obtained by Rietveld refinement using the equations from previous studies:

eq. I: 
$$\frac{c_t}{a_t} = 1.44289 - 0.00161X$$
 ..... (Toraya, 1989, Matsui et al, 2022)  
eq. II:  $\frac{c_t}{\sqrt{2}a_t} = 1.0223 - 0.001319X$  ..... (Miller et al, 1981, Belli et al, 2021)  
eq. III:  $\frac{c_t}{\sqrt{2}a_t} = 1.0225 - 0.0016X$  ..... (Pandoleon et al, 2017)

where  $a_t$  and  $c_t$  are the lattice parameters of a tetragonal unit cell in the aaxis and c-axis directions, respectively, and X is the YO<sub>1.5</sub> concentration in mol%. The yttria content inside the cubic phase was estimated from the lattice parameter obtained by Rietveld refinement using the equation from previous studies:

 $c_c = 0.0016X + 5.1132$  ..... (Wei and Gremillard, 2018, Roitero et al, 2022)

where  $c_c$  is the lattice parameter of a cubic unit cell, and X is the YO<sub>1.5</sub> concentration in mol%. The average Y<sub>2</sub>O<sub>3</sub> concentration in mol% can be calculated from the following equation:

$$Y_2O_3 \text{ (mol\%)} = \left(\frac{\frac{X}{100}}{2 - \frac{X}{100}}\right) \times 100$$

where X is the YO<sub>1.5</sub> concentration in mol%. For additional comparison, assintered 3Y-TZP specimens were also analyzed before surface grinding and polishing in the same way.

#### II. 4. Flexural strength analysis

The biaxial flexural strength was tested in accordance with ISO 6872:2015 (ISO, 2015). The specimens were positioned and loaded at a crosshead speed of 1.0 mm/min with a universal testing machine (Instron 3365, Instron Co., Canton, MA, USA).

#### **II. 5. Microstructural analysis**

To assess the microstructure of zirconia, specimens were thermally etched for 15 min at 1500°C and sputter coated, then observed with a scanning electron microscope (SEM) (S4700, Hitachi, Tokyo, Japan) at ×30000 magnification with an accelerating voltage of 20 kV. The crystal grain sizes were determined by using the linear intercept method in ASTM E112-10:2013 according to ISO 13356:1997, and 3-dimensional mean grain size was obtained from the measured values multiplied by a proportionality constant of 1.56 (ASTM, 2013, ISO, 1997, Mendelson, 1969).

#### II. 6. Density analysis

The density of the specimens was measured by using the Archimedes method in water, following the ISO 18754:2013 (ISO, 2013).

#### II. 7. Statistical analysis

Descriptive statistics using means and standard deviations calculated from the measured translucency, flexural strength, and mean grain size of each group were analyzed. The normality and equality of variances were assessed by using the Shapiro–Wilk and Levene tests. Individual one-way ANOVAs and Welch ANOVAs were conducted, and a post-hoc pairwise comparison was adjusted by using Bonferroni method ( $\alpha = .05$ ). All data analyses were performed by using a statistical software program (IBM SPSS Statistics v26; IBM Corp., Armonk, NY, USA) ( $\alpha = .05$ ), and statistical significance was denoted by P < .05.

# **III. RESULTS**

Translucency, biaxial flexural strength, mean grain size, density, and phase fraction were summarized for groups sintered for 2 hours at different sintering temperatures (Table 1 and Table 2) and for groups sintered at 1570°C for different holding times (Table 3 and Table 4). The results were also presented in graphical forms (Fig. 2 to Fig. 5). X-ray diffraction patterns were shown (Fig. 6B). For groups sintered for 2 hours at different sintering temperatures, as the sintering temperature increased, translucency and mean grain size significantly increased (P < .05), t-phase fraction decreased, c- and t"-phase fractions increased. Small amounts of m- and rphase fractions were observed. Flexural strength was not significantly different among the groups. For groups sintered at 1570°C for different holding times, as the holding time increased, mean grain size significantly increased (P < .05). Translucency was not significantly different among the groups, except for 1570°C-2h group (P < .05). Flexural strength was not significantly different among the groups. *c*-phase fraction increased from 2to 15-hour holding time and slightly decreased to 20-hour holding time. As holding time increased, t-phase fraction decreased and t''-phase fraction increased. Small amounts of *m*- and *r*-phase fractions were observed. Compared to the theoretical density of  $6.10 \text{ g/cm}^3$ , all groups showed nearly full density with more than 99% of the theoretical value. For all groups, a peak around 29.4 degrees, representing the presence of yttria  $(Y_2O_3)$ , was

not observed.

Table 1. Mean  $\pm$  standard deviation of translucency, flexural strength, and mean grain size, and density of groups sintered for 2 hours at different sintering temperatures

Group	Translucency (%)	Flexural strength (MPa)	Mean grain size (μm)	Density (g/cm³)
1500°C-2h	$42.0\pm0.5^{\rm a}$	$1436.3\pm275.5^{\text{d}}$	$0.427\pm0.010^{\text{e}}$	6.04
1550°C-2h	$43.0\pm0.4^{b}$	$1479.6\pm212.8^{\rm d}$	$0.560\pm0.014^{\rm f}$	6.06
1570°C-2h	$43.0\pm0.3^{b}$	$1428.2\pm335.3^{\text{d}}$	$0.634\pm0.019^{\text{g}}$	6.07
1600°C-2h	$43.5\pm0.5^{\rm c}$	$1463.3\pm251.5^{\rm d}$	$0.724\pm0.020^{\rm h}$	6.08
Different	letters within e	each column indicate	e statistically sig	mificant

Different letters within each column indicate statistically significant differences at P < .05.

**Table 2.** Crystalline phase fraction of groups sintered for 2 hours at different sintering temperatures

Group		A	s-sinter	ed		Polished				
	t (%)	ť" (%)	т (%)	r (%)	с (%)	t (%)	t" (%)	т (%)	r (%)	с (%)
1500°C-2h	82.4	4.3	0.5	0	12.9	79.7	8.0	0.7	0.9	10.7
1550°C-2h	80.4	4.5	0.0	0	15.0	78.0	8.5	0.8	1.4	11.3
1570°C-2h	79.3	3.4	0.1	0	17.3	75.5	9.0	0.7	1.9	13.0
1600°C-2h	75.4	3.8	0.0	0	20.8	74.3	9.7	0.7	1.7	13.6

t, tetragonal phase fraction; t'', tetragonal double-prime phase fraction; m, monoclinic phase fraction; r, rhombohedral phase fraction; c, cubic phase fraction.

Group	Translucency (%)	Flexural strength (MPa)	Mean grain size (µm)	Density (g/cm³)
1570°C-2h	$43.0\pm0.3^{\rm a}$	$1428.2\pm335.3^{\circ}$	$0.634\pm0.019^{\text{d}}$	6.07
1570°C-5h	$43.7\pm0.2^{b}$	$1659.4\pm204.6^{\circ}$	$0.739\pm0.020^{\text{e}}$	6.06
1570°C-10h	$44.0\pm0.2^{b}$	$1501.0\pm579.2^{\circ}$	$0.905\pm0.013^{\rm f}$	6.06
1570°C-15h	$43.6\pm0.2^{\text{b}}$	$1435.7 \pm 184.2^{\circ}$	$1.071\pm0.032^{\text{g}}$	6.06
1570°C-20h	$43.8\pm0.6^{\text{b}}$	$1440.0\pm293.5^\circ$	$1.184\pm0.028^{h}$	6.05

**Table 3.** Mean  $\pm$  standard deviation of translucency, flexural strength, and mean grain size, and density of groups sintered at 1570°C for different holding times

Different letters within each column indicate statistically significant differences at P < .05.

**Table 4.** Crystalline phase fraction of groups sintered at 1570°C for different holding times

Group		A	s-sinter	ed		Polished				
	t (%)	t" (%)	т (%)	r (%)	с (%)	t (%)	t" (%)	т (%)	r (%)	с (%)
1570°C-2h	79.3	3.4	0.1	0.0	17.3	75.5	9.0	0.7	1.9	13.0
1570°C-5h	76.6	4.3	0.7	0.0	18.5	73.7	9.8	0.7	2.0	13.8
1570°C-10h	69.4	4.7	6.3	1.0	18.7	71.5	10.2	1.0	2.1	15.2
1570°C-15h	59.5	7.8	14.5	5.0	13.3	70.3	10.1	0.8	2.6	16.2
1570°C-20h	44.4	7.7	25.8	10.8	11.3	69.7	10.5	1.3	2.6	16.0

t, tetragonal phase fraction; t'', tetragonal double-prime phase fraction; m, monoclinic phase fraction; r, rhombohedral phase fraction; c, cubic phase fraction.



**Figure 2.** Translucency. A, Groups sintered for 2 hours at different sintering temperatures. B, Groups sintered at 1570°C for different holding times.



Figure 3. Flexural strength. A, Groups sintered for 2 hours at different sintering temperatures. B, Groups sintered at 1570°C for different holding times.



Figure 4. Mean grain size. A, Groups sintered for 2 hours at different sintering temperatures. B, Groups sintered at 1570°C for different holding times.



Figure 5. Crystalline phase fraction for zirconia polymorphs of groups. t, tetragonal phase fraction; t'', tetragonal double-prime phase fraction; m, monoclinic phase fraction; r, rhombohedral phase fraction; c, cubic phase fraction.



Figure 6. X-ray diffraction pattern showing peaks for crystalline phases of zirconia. A, As-sintered specimen. B, Polished specimen. t, tetragonal phase; t'', tetragonal double-prime phase; m, monoclinic phase; r, rhombohedral phase; c, cubic phase.

A plot relating translucency and *c*-phase fraction was shown (Fig. 7). *c*-phase fraction of 10.7% showed the lowest translucency and no significant differences in translucency for *c*-phase fraction above 13.6%.



**Figure 7.** Plot relating translucency and cubic phase fraction. Different letters indicate statistically significant differences at P < .05.

Lattice parameters  $a_t$  and  $c_t$ , and tetragonality, calculated as  $\frac{c_t}{\sqrt{2}a_t}$ , for tetragonal unit cell, lattice parameter  $c_c$  for cubic unit cell, and yttria (Y<sub>2</sub>O<sub>3</sub>) content of tetragonal and cubic phases were summarized (Table 5 and Table 6). The results were also presented in graphical forms (Fig. 8 to Fig. 10). As the sintering temperature and holding time increased, the tetragonality of the tetragonal phase increased, thus birefringence increased, and yttria content of the tetragonal phase decreased, meaning migration of yttria from tetragonal grain interior to grain boundary and its segregation. Yttria content of the cubic phase increased as sintering temperature increased, meaning the inflow of yttria to cubic grain. As holding time increased, the yttria content of the cubic phase maintained from 5- to 20hour holding time, meaning no release of yttria from cubic grain.

Group		Cubic phase						
	at	$\mathbf{c}_t$	Tatua	Y	2O3 (mo	l%)	a (l)	Y2O3
	(Å)	(Å)	Tetragonanty	Eq I.	Eq. II	Eq. III	C <sub>c</sub> (A)	(mol%)
1500°C-2h	3.6052	5.1778	1.0155	2.12	2.63	2.22	5.1285	4.61
1550°C-2h	3.6052	5.1788	1.0157	2.03	2.55	2.16	5.1292	4.84
1570°C-2h	3.6049	5.1789	1.0158	1.98	2.51	2.12	5.1304	5.23
1600°C-2h	3.6048	5.1792	1.0159	1.95	2.47	2.10	5.1314	5.57

**Table 5.** Lattice parameters, tetragonality, yttria  $(Y_2O_3)$  concentration of tetragonal and cubic phases for groups sintered for 2 hours at different sintering temperatures

 $a_t$ , lattice parameter in a-axis direction of tetragonal unit cell;  $c_t$ , lattice parameter in c-axis direction of tetragonal unit cell;  $c_c$ , lattice parameter of cubic unit cell.

**Table 6.** Lattice parameters, tetragonality, yttria  $(Y_2O_3)$  concentration of tetragonal and cubic phases for groups sintered at 1570°C for different holding times

Group		Cubic phase						
	a <sub>t</sub>	<b>c</b> <sub>t</sub>	Y2O3 (mol%)				<b>c</b> <sub>c</sub>	Y2O3
	(Å)	(Å)	Tetragonality -	Eq I.	Eq. II	Eq. III	(Å)	(mol%)
1570°C-2h	3.6049	5.1789	1.0158	1.98	2.51	2.12	5.1304	5.23
1570°C-5h	3.6046	5.1795	1.0161	1.88	2.42	2.05	5.1315	5.58
1570°C-10h	3.6043	5.1800	1.0162	1.81	2.35	2.00	5.1313	5.51
1570°C-15h	3.6042	5.1802	1.0163	1.78	2.33	1.98	5.1317	5.65
1570°C-20h	3.6041	5.1803	1.0164	1.75	2.30	1.96	5.1313	5.53

 $a_t$ , lattice parameter in a-axis direction of tetragonal unit cell;  $c_t$ , lattice parameter in c-axis direction of tetragonal unit cell;  $c_c$ , lattice parameter of cubic unit cell.



**Figure 8.** Lattice parameters  $a_t$  and  $c_t$  of tetragonal unit cell. A, Groups sintered for 2 hours at different sintering temperatures. B, Groups sintered at 1570°C for different holding times.



**Figure 9.** Tetragonality of tetragonal unit cell. A, Groups sintered for 2 hours at different sintering temperatures. B, Groups sintered at 1570°C for different holding times.



Figure 10. Lattice parameter  $c_c$  of cubic unit cell. A, Groups sintered for 2 hours at different sintering temperatures. B, Groups sintered at 1570°C for different holding times.

SEM images corresponding to the groups were shown (Fig. 11 and Fig. 12). As the sintering temperature and holding time increased, an increase in the number of cubic grains and an increase in cubic grain size were prominently observed. The mean grain size increased as *c*-phase fraction increased.



**Figure 11.** SEM images (magnification ×30000) of groups sintered for 2 hours at different sintering temperatures. A, 1500°C-2h. B, 1550°C-2h. C, 1570°C-2h. D, 1600°C-2h.



**Figure 12.** SEM images (magnification ×30000) of groups sintered at 1570 °C for different holding times. A, 1570 °C-5h. B, 1570 °C-10h. C, 1570 °C-15h. D, 1570 °C-20h.

X-ray diffraction patterns and phase fraction of zirconia polymorphs for all groups in as-sintered and polished states were shown (Table 2 and Table 4) (Fig. 6 and Fig. 13). For groups sintered for 2 hours at different sintering temperatures, *t*- and *c*-phase fraction decreased and *t*"- and *r*-phase fraction increased after grinding and polishing. For groups sintered at  $1570^{\circ}$ C for different holding times, by the grinding and polishing, *t*-phase fraction decreased for 2- and 5-hour holding time and *c*-phase fraction decreased for 2-, 5-, and 10-hour holding time. Considerable amounts of *m*and *r*-phase fractions were observed in an as-sintered state for 10- to 20hour holding times, and, by the grinding and polishing, *m*- and *r*-phase fractions decreased, and *t*- and *c*-phase fractions increased.



Figure 13. Phase fraction for zirconia polymorphs of groups. For each group, left bar is for as-sintered specimen, and right bar is for polished specimen. t, tetragonal phase fraction; t'', tetragonal double-prime phase fraction; m, monoclinic phase fraction; r, rhombohedral phase fraction; c, cubic phase fraction.

# **IV. DISCUSSION**

Based on the results of this study, phase fraction and mean grain size significantly affected the translucency of 3Y-TZP, supporting the research hypothesis. Translucency increased as c-phase fraction increased and was saturated above *c*-phase fraction of 13.6%. Translucency increased as the mean grain size increased and was saturated above a mean grain size of 0.724 µm. Translucency increased as the sintering temperature increased and was not affected by the increase in holding time. Translucency is the optical phenomenon resulting from various contributing factors. Increases in *t*-phase fraction or tetragonality of *t*-phase negatively affect translucency. Increases in *c*- or *t*"-phase fractions positively affect translucency. *c*-phase is isotropic and has no birefringence, and t"-phase has low birefringence with tetragonality close to 1, while t-, m-, and r-phases are anisotropic and have birefringence. *m*-phase was known to act as a flaw or defect; thus, decreases translucency (Kohorst et al, 2012, Fischer and Marx, 2002, Fathy et al, 2015). Mean grain size is the result of the quantity and size of the zirconia polymorphs; thus, the effect on translucency was not fully understood yet. For groups sintered for 2 hours at different sintering temperatures, as the sintering temperature increased, translucency significantly increased (P < .05), as a result of balance among increased mean grain size, decreased tphase fraction with increasing birefringence, and increased c- and t''-phase fractions. Decreased *t*-phase fraction and increased *c*- and *t*"-phase fractions

would have dominantly affected the translucency. For groups sintered at 1570°C for different holding times, as the holding time increased, translucency was not significantly different among the groups, except for 1570°C-2h group (P < .05), as a result of balance among increased mean grain size, decreased *t*-phase fraction with increasing birefringence, and increased *c*-phase fraction (2- to 15-hour holding time) and *t*"-phase fraction. Increased birefringence of *t*-phase would have offset the effect of positively contributing factors. Holding time longer than 5 hours at 1570°C did not increase the translucency nor flexural strength, even with the phase fraction change, and thus had inefficiency in specimen fabrication. Overall, translucency cannot be simply explained or predicted only by a specific single factor; rather, it should be explained with all contributing factors.

Cubic grain has a larger size than tetragonal grain. From the SEM images, the increase in mean grain size as sintering temperature and holding time increase attributed more to the increase in the number of cubic grains and the increase in cubic grain size than to the increase in tetragonal grain size. The mean grain size was closely related to *c*-phase fraction from the present study. The linear intercept method used to calculate mean grain size did not distinguish tetragonal and cubic grains. For a given zirconia powder, sintering temperature and time are major factors to affect the grain size. Grain size increases as sintering temperature increases (Stawarczyk et al, 2013, Darmawan et al, 2020, Kilinc and Sanal, 2021, Cardoso et al, 2020), or sintering time increases (Chevalier, 2004, Denry and Kelly, 2008, Ebeid

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et al, 2014), same as the result of the present study. In general, higher sintering temperature leads to pore elimination, which leads to increased translucency, as well as grain size increase (Gómez et al, 2016). As the sintering time increases, grain growth is suppressed by the segregation of yttria and is promoted by long holding time at final temperatures; thus, the grain size is determined by the balance between these factors (Nonaka et al, 2022, Matsui et al, 2009, Matsui et al, 2008). In the present study, an increase in mean grain size up to 0.724 nm had an effect on improving the translucency of 3Y-TZP by reducing grain boundary scattering, as in previous studies (Denry and Kelly, 2014, Kilinc and Sanal, 2021, Ebeid et al, 2014, Jiang et al, 2011, Sen et al, 2018, Stawarczyk et al, 2013). From the present study, the effect of grain size on translucency was unclear, which necessitates further research.

Factors to decrease translucency are known as grain boundaries, pores, and scattering from rough surfaces (Kim et al, 2013). It was reported that the effect of density is greater than the effect of grain size on translucency since more scattering occurs from micropores than from grain boundaries (Pekkan et al, 2020, De Souza et al, 2008). A previous study reported that the tendency of translucency was consistent with density, and density was the main factor to affect the translucency of 3Y-TZP (Jiang et al, 2011). Increasing the density is an effective way to improve translucency (Zhang, 2014). It was also reported that, for the grain size with submicron, scattering from the internal pore decreases significantly (Kim et al, 2013). In

this study, all groups showed nearly full density, and grain sizes were submicron; thus, the effect of pores or defects could have been considered minimized. All groups did not show any hollow hole formation, crack formation, or decrease in density for higher sintering temperatures, as in the previous study (Stawarczyk et al, 2013).

Flexural strength was not affected by phase fraction, mean grain size, sintering temperature, and holding time. The large grain size was known to compromise the strength of ceramics (Rice, 1997, Chantikul et al, 1990, Pekkan et al, 2020). For zirconia, high strength and toughness are attributed to t to m phase transformation, but c-phase or t''-phase does not contribute to stress-induced transformation toughening. A large portion of *c*phase sacrifices the strength and toughness of Y-TZP. Unlike t-phase, t"phase, which originated from *c*-phase by an ordering mechanism of an anionic sublattice, does not undergo phase transformation to *m*-phase (Cairney et al, 2007, Yashima et al, 1993, Belli et al, 2021). For groups sintered for 2 hours at different sintering temperatures, as the sintering temperature increased, flexural strength was not significantly different among the groups, as a result of balance among increased mean grain size, decreased fraction for *t*-phase contributing transformation toughening but not below 70%, a small amount of *m*-phase fraction maintained, and increased c- and t"-phase fractions. For groups sintered at 1570°C for different holding times, as the holding time increased, flexural strength was not significantly different among the groups, as a result of balance among increased mean grain size, decreased *t*-phase fraction but not below 70%, a small amount of *m*-phase fraction maintained, and increased *c*- and *t*"-phase fractions. *t*-phase fraction greater than 70% would have dominantly affected the flexural strength than the mean grain size and *c*- and *t*"-phase fractions. It was reported that strength was significantly decreased when the *m*-phase fraction was over 50% in a previous systematic review (Pereira et al, 2015).

By the grinding and polishing for the as-sintered specimens, decreased *t*- and *c*-phase fractions and increased fraction for *t*"-phase, which would have been transformed from *c*-phase by the stress, were observed. For groups sintered at 1570°C for 10- to 20-hour holding times, due to the long holding time, considerable amounts of fraction for *m*-phase, which would have been transformed from *t*-phase, and fraction for *r*-phase, which would have been transformed from *c*-phase, were observed. As the grain size increases, the stress in the grain increases, thus resulting in spontaneous phase transformation, which was not desirable. Considerable amounts of mand r-phase fractions were substantially decreased by the grinding and polishing. Increases in t-phase fraction for 10-, 15-, and 20-hour holding time, and *c*-phase fraction for 15- and 20-hour holding time after grinding and polishing were due to the base effect of the considerable amounts of mand *r*-phase fractions for as-sintered specimens.

The previous studies reported that yttria diffuses from a tetragonal phase in grain interiors to the grain boundaries, and yttria segregates in the grain boundaries, resulting in uneven yttria distribution with the formation of high-yttria tetragonal phase near grain boundaries or cubic phase at grain boundaries (Matsui et al, 2022, Stawarczyk et al, 2013, Scott, 1975, Denry and Kelly, 2008, Chevalier, 2004). In the present study, decreased yttria content of the tetragonal phase and increased yttria content of cubic phase as sintering temperature increased, and decreased yttria content of the tetragonal phase and maintained yttria content of the cubic phase as holding time increased, were observed. The migration of yttria from tetragonal grain interior to grain boundary, its segregation in the grain boundaries, and inflow to cubic grain could be inferred.

Although the presence of the cubic phase of 3Y-TZP at room temperatures is still in dispute, there is no evidence to prove or refute the presence of cubic phase of 3Y-TZP at room temperature, and recent studies revealed the presence of cubic phase of 3Y-TZP at room temperatures (Matsui et al, 2022, Belli et al, 2021, Nonaka et al, 2022). In the present study, *c*-phase was included for analysis with Rietveld refinement. From the X-ray diffraction patterns for as-sintered specimens, broadening and asymmetry of the peak near 30.2 degrees were obviously observed due to other crystalline phases (*c*, *t*", and *r*).

To measure the translucency, 3 common methods, namely light transmittance, translucency parameter (TP), and contrast ratio (CR) methods, are used (Pekkan et al, 2020). For light transmittance, direct transmission, total transmission, and indirect measurements via spectral reflectance can be used (Kim et al, 2013). In this study, we assessed translucency by the direct transmission method, which measures the light that reaches a detector passing through the specimens.

This study had several limitations. X-ray diffraction analysis showed the crystalline phase fraction of the surface only. X-ray photoelectron spectroscopy (XPS) depth profiling would be necessary. The independent effects of individual contributing factors on translucency were not assessed. Changing the sintering parameters (sintering temperature and holding time) is a simple and convenient method to change translucency, but it changes many contributing factors simultaneously; thus, it was hard to distinguish the effect of individual contributing factors on translucency. Limited ranges of sintering temperatures and holding times were utilized for the analysis. Second, quantitative analysis for contributing factors was limited. Interpretation of the result for the effect of crystalline phase fraction translucency and strength was made qualitatively rather than on quantitatively, which necessitates further research. Analysis for metastability and low-temperature degradation susceptibility is necessary to assess the long-term integrity of 3Y-TZP.

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# **V. CONCLUSIONS**

Based on the findings of this in vitro study, translucency was affected by all contributing factors, including crystalline phase fractions, mean grain size, tetragonality of the tetragonal phase, and density. Increased *c*- or *t*"-phase fractions and *t*-phase fraction above critical level by suppressing other undesired phases would improve the translucency without compromising the strength and toughness of 3Y-TZP.

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### 국문 초록

# 3Y-TZP 지르코니아 결정상 분율과 입자 크기가 투광도에 미치는 영향

서울대학교 대학원 치의과학과 치과보철학 전공

(지도교수 한 중 석)

# 조 준 호

목적. 본 연구는 3Y-TZP 지르코니아 동소체 결정상 분율과 입자 크기가 투광도에 미치는 영향을 평가하고자 하였다.

재료 및 방법. 알루미나 성분을 포함하지 않는 지르코니아 (3Y-TZP) 분말을 이용하여 cold isostatic pressing (CIP) 기술로 디 스크 형태의 시편을 성형하였다. 최종 소결 온도와 최종 소결 온 도에서의 유지 시간을 기준으로 다음의 8개의 그룹으로 분류하였 다 (n = 10): 1500℃-2h, 1550℃-2h, 1570℃-2h, 1600℃-2h, 1570℃-5h, 1570℃-10h, 1570℃-15h, 1570℃-20h. 각각의 소결 온도와 시간에 따라 소결을 진행하였고, 소결된 시편은 최종 적으로 직경 14.0 mm, 두께 1.0 mm가 되도록 양면 그라인딩 및 폴리싱을 거쳤다. 투광도, 2축 굴곡강도, 밀도를 측정하였다. 주사 전자현미경(SEM)을 통해 미세구조를 관찰하고, 평균 입자 크기를 계산하였다. X선 회절법 및 Rietveld refinement를 이용하여 지르 코니아 동소체 결정상 분율 및 unit cell의 격자상수를 분석하였다. 일원배치 분산분석, Welch 분산분석, 사후 검정을 통해 통계적 분 석을 시행하였다 (α = .05).

결과. 소결 온도가 증가함에 따라 투광도와 평균 입자 크기는 유 의하게 증가하였고 (P < .05), t상 분율은 감소, c상 및 t"상 분율 은 증가하였다. 유지 시간이 증가함에 따라 투광도는 1570℃-2h 그룹을 제외하고는 (P < .05) 그룹 간 유의한 차이가 없었고, 평 균 입자 크기는 유의하게 증가하였으며 (P < .05), t상 분율은 감 소, t"상 분율은 증가하였다. c상 분율은 유지 시간이 2시간에서 15시간까지는 증가하다가 20시간에 이르러 약간 감소하였다. 굴 곡강도는 소결 온도 및 유지 시간에 따라 그룹 간 유의한 차이가 없었다. 모든 그룹에서 이론값의 99% 이상의 밀도를 가졌다. 소 온도 및 유지 시간이 증가함에 따라 t상의 정방성 결 (tetragonality)은 증가하였고, t상의 이트리아 함량은 감소하였다. 소결 온도가 증가함에 따라 c상의 이트리아 함량은 증가하였고, 유지 시간이 5시간에서 20시간까지는 비슷한 수준으로 유지되었 다. 동일한 시편의 그라인딩 및 폴리싱이 되지 않은 상태와 비교 할 때, 그라인딩 및 폴리싱 과정에 의해 t상과 c상 분율은 갂소하

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였고, t"상과 r상 분율은 증가하였다.

결론. 본 연구를 통해 3Y-TZP의 투광도는 결정상 분율, 평균 입 자 크기, *t*상의 정방성, 밀도를 포함하는 모든 기여 요인들에 의해 영향을 받으며, 증가된 *c*상 및 *t*"상 분율, 임계 수준 이상의 *t*상 분율, 원하지 않는 상의 분율 최소화를 통해 강도와 인성을 감소 시키지 않으면서 3Y-TZP의 투광도를 향상시킬 수 있다.

**주요어:** 3Y-TZP; 투광도; 결정상 분율; 지르코니아 동소체;

입자 크기; 굴곡강도

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