

# Effect of Coloring on Mechanical Properties of Dental Zirconia

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## Abstract

Pre-sintered blocks of three kinds of yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) and one ceria-stabilized tetragonal zirconia polycrystal (Ce-TZP)/alumina nanocomposite were stained with six kinds of coloring liquid (three ivory, two violet, and one pink). The crystal phases of the baking powder of the coloring liquids fired at 1100 °C for 30 min were characterized by X-ray diffractometry (XRD) and their constituent elements were detected by wavelength dispersive X-ray spectroscopy (WDS). The three ivory liquids contained mainly Fe ions, the two violet liquids mainly contained Co ions, and the pink liquid contained Er and Nd ions. After the final sintering, the color differences ( $\Delta E$ ) were determined with a chroma meter. Three-point flexural strengths were determined at a span length of 16 mm according to ISO 6872. Fracture toughness was determined by an indentation method in terms of Palmqvist cracks. The color difference of the nanocomposite was smaller than those of three Y-TZPs due to high light scattering. The three ivory liquids for the nanocomposite led to small  $\Delta E$  values. The sintered zirconia stained with the pink liquid containing Er and Nd ions showed significant decreases in flexural strength and fracture toughness. An XRD study revealed that most of the crystal phase of the zirconia stained with Er and Nd was cubic. In contrast, the three ivory and two violet liquids led to no significant change in the flexural strength and fracture toughness of the zirconia.

**Keywords:** Zirconia, Dentistry, Coloring, Color difference, Flexural strength, Fracture toughness

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## 1. Introduction

Zirconia is used for dental restoratives such as crowns, bridges, implant fixtures, implant abutments, and brackets [1] due to its suitable properties for dental prostheses [2-7]. The excellent mechanical properties of zirconia are due to the stress-induced transformation toughening mechanism, similar to that in quenched steel. The transformation from the tetragonal phase to the monoclinic phase occurs via a diffusionless shear process at near-sonic velocities, similar to those of martensite formation in quenched steel [8]. Yttria-stabilized tetragonal zirconia polycrystals (Y-TZPs) have been increasingly applied to dental restoratives using computer-aided design/computer-aided manufacturing (CAD/CAM) systems [1,9]. Dental CAD/CAM systems generally manufacture pre-sintered blocks to reduce machining time and

the wear of machining tools. After machining, the blocks must be fired at the given firing temperatures according to the manufacturer's directions. The disadvantages of zirconia are its low translucency and milky-white color. Coloring the zirconia to match a patient's requirements for esthetic tooth reconstruction is thus essential. The surface of the zirconia core is generally covered with veneering feldspathic porcelain after the final firing. However, the strength of the veneering porcelain is insufficient for dental restoratives [1]. The chipping of the porcelain has been reported [10,11]. Recently, the translucency of dental zirconia has been improved. The highly translucent zirconia was developed by decreasing the light scattering sources, such as alumina particles, without significantly affecting its mechanical properties [12]. With highly translucent zirconia, the veneering porcelain is unnecessary and the surface of zirconia is exposed in the oral cavity. This restorative framework is called "full contour". The coloring of zirconia itself is required for enhancing its esthetics. After CAD/CAM processing, adequate coloring liquids are painted onto the machined/pre-sintered blocks with brush, dried, and finally sintered at high temperature (1350-1600 °C).

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Various metal ions are used in these coloring liquids [13-18]. For instance, iron (Fe) is used for brown, erbium (Er) is used for light violet, neodymium (Nd) is used for light pink, cerium (Ce) is used for cream and/or orange, terbium (Tb) is used for light orange, manganese (Mn) is used for black, and praseodymium (Pr) is used for dark yellow [17]. The various ions in the coloring liquid may act as impurities in the sintered zirconia block and affect its properties. A few studies have found that coloration decreased the flexural strength of zirconia [13,19], but a few found no effects [14]. Furthermore, it is known that coloration is independent of the action or soaking time of the solution, depending only on the concentration [16]. Colored zirconia can also be obtained by adding small amounts of metal oxides to the starting powder [18]. In the present study, the properties of dental zirconia with various coloring liquids are evaluated through the measurement of the color difference, flexural strength, and fracture toughness. These results will help to improve the optical performance and mechanical durability of highly translucent zirconia for dental prostheses.

**2. Materials and methods**

*2.1 Zirconia and coloring liquids*

Four kinds of zirconia were used in this study, as shown in Table 1. P-NANOZR is a ceria-stabilized TZP and alumina nanocomposite (30 vol.% alumina) [20]. Cercon, ZENOSTAR, and Zirkozahn Prettau are Y-TZPs. ZENOSTAR and Zirkozahn Prettau are highly translucent. Plate-like specimens (5 × 25 × 1 mm) were cut from the pre-sintered blocks.

Table 1. Zirconia used in this study.

Name	Manufacturer	Composition	Final sintering (°C)
P-NANOZR	Panasonic Health Care	Ce-TZP/alumina nano-composite	1450
Cercon base	Dentsply		1350
ZENOSTAR Pure	Wieland	Y-TZP	1450
Zirkozahn Prettau	Zirkozahn		1600

*2.2 Coloring procedure*

The plates were immersed in six kinds of coloring liquid, shown in Table 2, for 30 min at room temperature and dried in air. The immersed plates were finally sintered for 2 h at 1350 °C for Cercon, at 1450 °C for P-NANOZR and ZENOSTAR, and at 1600 °C for Zirkozahn Prettau.

Table 2. Coloring liquid used in this study.

Code	Name	Manufacturer	Lot No.
I4	IPS e.max ZirCAD Coloring Liquid 4	Ivoclar Vivadent	N49042
W3	ZENOSTAR Color Zr A3.5	Wieland	060910
Z3	Color Liquid A3.5 Prettau	Zirkozahn	CB1115A
WV	Grey-Violet	Wieland	060510
ZV	Color Liquid Incisal Violet	Zirkozahn	CB0371B
ZB	Color Liquid Tissue B	Zirkozahn	CB0044B

*2.3 Measurement of properties*

$L^*$ ,  $a^*$ , and  $b^*$  were determined with a chroma meter (CR200, Minolta, Tokyo, Japan) on a white background. The color differences ( $\Delta E$ ) were derived from the differences in the values with ( $L_c^*$ ,  $a_c^*$ , and  $b_c^*$ ) and without coloring ( $L_o^*$ ,  $a_o^*$ , and  $b_o^*$ ) using the following equation:

$$E = [(L_c^* - L_o^*)^2 + (a_c^* - a_o^*)^2 + (b_c^* - b_o^*)^2]^{1/2} \tag{1}$$

Three-point flexural strengths were determined at a span length of 16 mm according to ISO 6872. Fracture toughness was determined by an indentation method in terms of Palmqvist cracks [21,22], not median cracks [23,24].

$$K_{IC} = 9.052 \cdot 10^{-3} \cdot H^{0.6} \cdot E^{0.4} \cdot d \cdot l^{-0.5} \tag{2}$$

where  $H$  is the hardness,  $E$  is the elastic modulus,  $d$  is the diagonal indentation length, and  $l$  is the crack length. The indentation was conducted using a Vickers hardness tester (HM-101, Akashi, Yokohama, Japan) under a 1-kg load for 15 s. For P-NANOZR, the crack lengths were determined with a scanning electron microscope (SEM, JXA-8530FA, JEOL, Tokyo, Japan) because they were too small to determine with an optical microscope.

*2.4 Characterization*

The coloring liquids were fired at 1100°C for 30 min to produce the powders for the following analysis. The crystal phases of these baking powders were characterized with an X-ray diffractometer (XRD, Ultima IV, Rigaku, Tokyo, Japan). Scans were conducted with Cu  $K\alpha$  radiation at 40 kV and 40 mA for  $2\theta$  angles in the range of 25° to 76° at 2°/min. The XRD patterns were qualitatively analysed using computer software (PDXL 2, Rigaku, Tokyo, Japan) and International Centre for Diffraction Data (ICDD). The constituent elements of the baking powder of the coloring liquid were detected by wavelength dispersive X-ray spectroscopy (WDS, JXA-8530FA, JEOL, Tokyo, Japan). Qualitative analyzes were conducted at 15 kV and  $4.8 \times 10^{-8}$  A. To detect all elements according to the previous reports [13-18,25,26], WDS spectra were scanned with four kinds of X-ray detector: Layered dispersion element (LDE1H), Thallium acid phthalate (TAP), Penta erythritol (PET), and Lithium fluoride (LiFH) crystals.

The crystal phase of the sintered zirconia plates (4 × 20 × 0.8 mm) with and without colorization were analyzed by XRD.

Element distribution maps of the sintered zirconia specimens were observed using WDS under the following operating conditions: applied voltage of 20 kV, filament current of  $5.0 \times 10^{-8}$  A, counting time of 20 ms, measurement area of  $256 \times 192$  pixels, and pixel size of  $0.1 \times 0.1$   $\mu$ m.

**3. Results**

*3.1 Composition of coloring liquids*

Figure 1 shows XRD patterns of the baking powders of the coloring liquids fired at 1100 °C for 30 min. The patterns

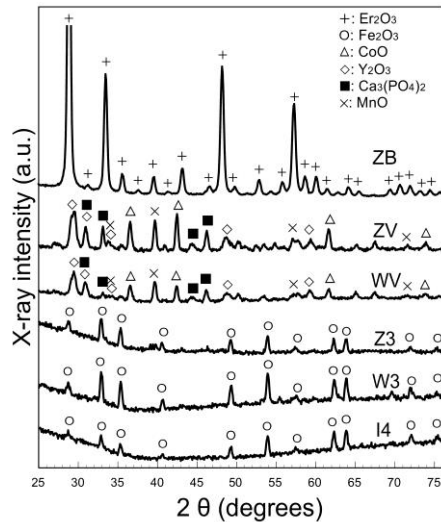


Figure 1. XRD patterns of baking powders of coloring liquids fired at 1100 °C.

for the three ivory liquids, namely A shade (I4, W3, and Z3), show only peaks corresponding to  $\text{Fe}_2\text{O}_3$ . Those for the two violet liquids (WV and ZV) show peaks corresponding to  $\text{CoO}$  and small amounts of  $\text{Y}_2\text{O}_3$ ,  $\text{Ca}_3(\text{PO}_4)_2$ , and  $\text{MnO}$ . That for ZB shows only peaks corresponding to  $\text{Er}_2\text{O}_3$ . Table 3 shows the crystal phases of the fired coloring liquids analyzed by XRD. Figure 2 shows WDS spectra of the baking powders of Z3, ZV, and ZB detected with LiFH. The spectra of I4 and W3 are similar to that of Z3 and that of WV is similar to that of ZV (data not shown). Table 4 summarizes the results of element analysis with the four kinds of X-ray detector.

Table 3. Crystal phase and their ICDD Number of the baking powders of the coloring liquid analysed by XRD.

Code	Crystal phase	ICDD No.
I4		
W3	$\text{Fe}_2\text{O}_3$	01-071-5088
Z3		
WV	$\text{CoO}$	01-070-2856
	$\text{Y}_2\text{O}_3$	01-074-1828
	$\text{Ca}_3(\text{PO}_4)_2$	01-086-1585
ZV	$\text{MnO}$	01-072-1533
ZB	$\text{Er}_2\text{O}_3$	01-077-0464

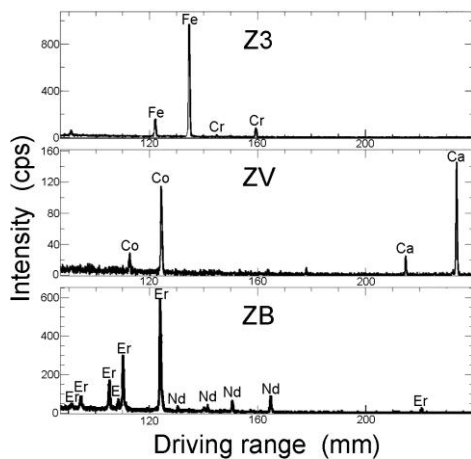


Figure 2. WDS spectra of baking powders of Z3, ZV, and ZB detected with LiFH.

Table 4. Constituent elements in the baking powders of the coloring liquid detected with four kinds of X-ray detector. Element in blank indicates relatively small amount.

Code	LDEIH	TAP	PET	LiFH
I4	O, Fe	Fe, P	Fe, Ca	Fe, (Cr)
W3	O, Fe	P, Y, (Al, Mg, Fe)	Fe, Ca, (P, Y)	Fe, (Cr)
Z3	O, Fe	(Fe)	Fe, Ca, (Y)	Fe, (Cr)
WV	O	Mg, (Y)	Ca, (Co, Mn)	Co, Ca, (Mn)
ZV	O	Y, P, Al	Ca, (P, Y)	Co, Ca
ZB	O	Er	Er	Er, (Nd)

### 3.2 Change in properties

Figure 3 shows the color difference ( $\Delta E$ ) of the four kinds of zirconia with and without coloring.  $\Delta E$  values of P-NANOZR are smaller than those of the Y-TZPs. The three ivory liquids for P-NANOZR led to quite small  $\Delta E$  values because the  $L$  value of P-NANOZR is larger than those of the Y-TZPs. The high light scattering depended on the mixture of alumina particles.

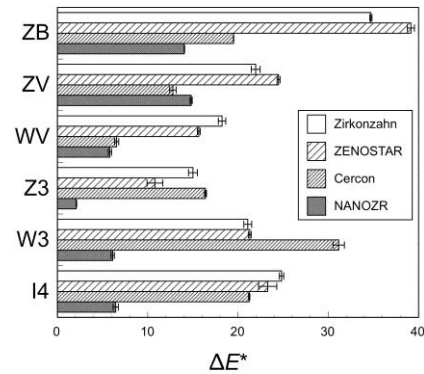


Figure 3. Color differences of four kinds of zirconia after coloring.

Figure 4 shows the three-point flexural strength of the four kinds of zirconia with and without coloring. P-NANOZR has larger strengths than those of the Y-TZPs for all coloring liquids. Color did not greatly affect the strength of zirconia except that of ZB. The strengths of zirconia were lost after coloring with ZB. Figure 5 shows the fracture toughness ( $K_{Ic}$ ) of Cercon and P-NANOZR with and without coloring.  $K_{Ic}$  values of Cercon calculated using equation (1), Palmqvist cracks [21,22], were about half those calculated using median cracks [23,24], whereas  $K_{Ic}$  values of P-NANOZR were similar for both calculations. P-NANOZR showed about three times larger value than Cercon except ZB. There were no significant

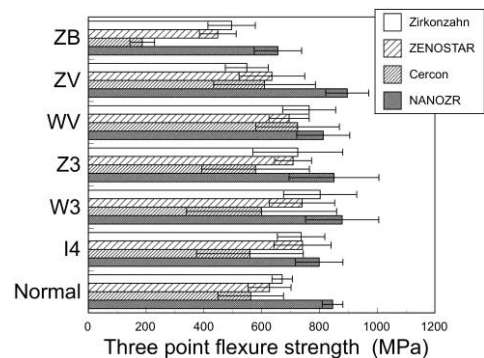


Figure 4. Three-point flexural strength of four kinds of zirconia with and without coloring.

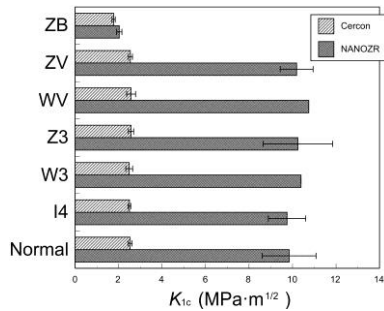


Figure 5. Fracture toughness of two kinds of zirconia with and without coloring.

differences in the  $K_{1c}$  values with and without coloring except those for ZB. The  $K_{1c}$  values of ZB for both P-NANOZR and Cercon were smallest. The behaviours for fracture toughness are similar to those for three-point flexural strength.

### 3.3 Change in microstructure

Figures 6-9 show XRD patterns of the four zirconia with and without coloring. There are no remarkable differences in the XRD patterns with and without coloring except those for ZB. Most of these patterns were assigned to tetragonal zirconia (ICDD No. 01-083-0113). The XRD patterns of all the zirconia after coloring with ZB showed the formation of cubic-phase zirconia (ICDD No. 01-078-1307). Figure 10 shows element distribution maps of zirconium (Zr), erbium (Er), and neodymium (Nd) together with a secondary electron image (SEI) of the surface of ZENOSTAR after coloring with ZB. The concentrations of Er and Nd increased in the large grains and that of Zr decreased. Judging from the XRD study, these large grains may be the cubic phase.

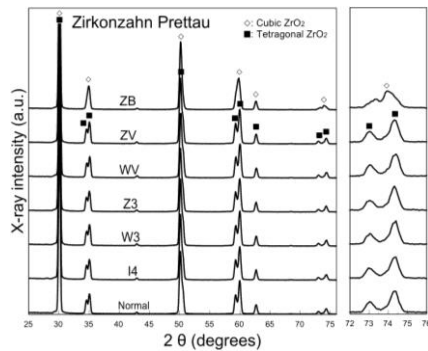


Figure 6. XRD patterns of Zirkonzahn Prettau with and without coloring.

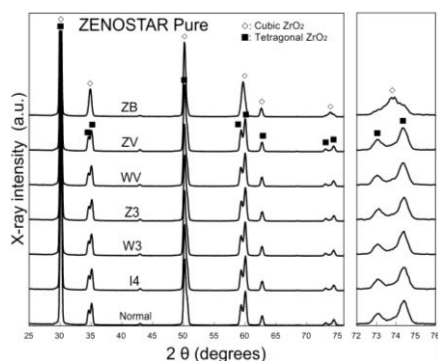


Figure 7. XRD patterns of ZENOSTAR with and without coloring.

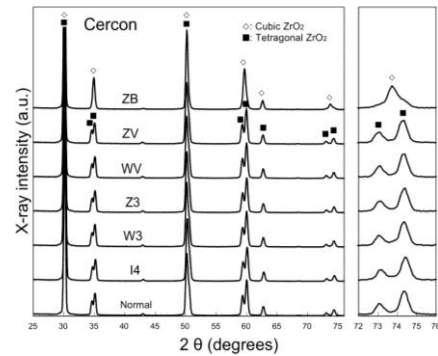


Figure 8. XRD patterns of Cercon with and without coloring.

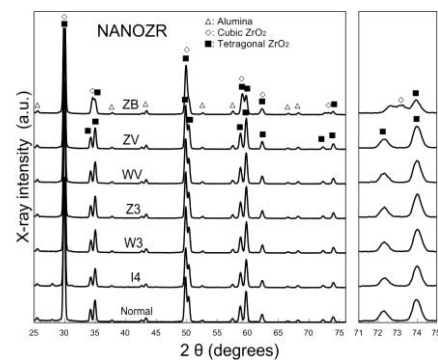


Figure 9. XRD patterns of P-NANOZR with and without coloring.

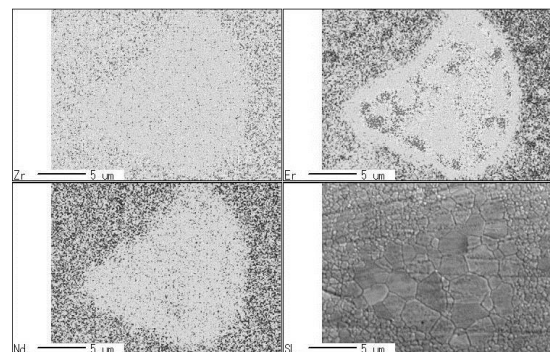


Figure 10. Element distribution maps of zirconium (Zr), erbium (Er), and neodymium (Nd) together with SEI (SL) of the surface of ZENOSTAR after coloring with ZB.

## 4. Discussion

In comparison to the XRD pattern of the zirconia without coloring (normal firing), no diffraction peaks assigned to  $Fe_2O_3$  and  $CoO$  were observed in the XRD patterns of the fired zirconia with coloring liquids except for those with ZB, although the diffraction peaks due to  $Fe_2O_3$  and  $CoO$  were clearly detected in the baking powder of these coloring liquid. It seems that the content of these ions in the sintered zirconia after the firing was too small to be detected by XRD. A small amount of these ions contributed the coloration of zirconia.

According to the analytical results of the baking powder of the coloring liquids shown in Tables 3 and 4, the three kinds of ivory liquid (I4, W3 and Z3) mainly consist of Fe ions and a small number of Cr ions, the two violet liquids (WV and ZV) mainly consist of Co ions and small amounts of Ca, Y, Mn, and P, and ZB mainly consists of Er ions and a small number of Nd

ions. These analytical results were obtained for the baking powders of the coloring liquids fired at 1100 °C for 30 min. According to previous papers [13-15], these ions appear in the liquids as acetate, chloride, nitrate, and alcohol solutions as well as oxo complexes. After drying, at the initial stage of heating after immersion to porous pre-sintered zirconia block, the anions (acetic, chloric, and nitric ions) probably burned out or vaporized, and disappeared on the surface of the pores of the zirconia block. The metal ions formed an oxide layer on the surface of the pores of the zirconia block. Because the blocks were pre-sintered at 1000-1100 °C after being pressed, no sintering occurred below the pre-sintering temperature. It can be assumed that these metal ions rarely reacted with zirconia below the pre-sintering temperature. This means that these metal oxides formed a new product with zirconia via a solid-solid reaction or remained as oxides at the boundaries around zirconia grains in the final sintering stage (1350-1600 °C). This is the reason why the baked oxide powders of the coloring liquid were analyzed in the present study.

XRD peaks assigned to the cubic phase were clearly observed after coloring with ZB, as shown in Figs. 6-9, regardless of the stabilization element (Y or Ce). The formation of the cubic phase resulted in a reduction of the flexural strength and fracture toughness. It is well known that cubic zirconia is weaker than tetragonal zirconia, because the stable cubic zirconia is impossible to be strengthened by the stress-induced transformation [16].

As shown in Table 4, ZB contained Er and Nd ions. It is known that both Er and Nd act as stabilizers for cubic zirconia [27,28], creating a large strain in the crystal lattice due to their substitutions because the ionic radii of  $Zr^{4+}$ ,  $Y^{3+}$ ,  $Er^{3+}$ , and  $Nd^{3+}$  are 0.084, 0.1019, 0.1004, and 0.1109 nm, respectively [29]. As mentioned above, the formation of the cubic phase resulted in a decrease in the flexural strength and fracture toughness. These results suggest that coloring liquids containing Er and/or Nd should be avoided for dental prostheses. Furthermore, coloring with Fe and Co showed no remarkable property changes, indicating little reaction with zirconia and the formation of each oxide at grain boundaries. Although no diffraction peaks assigned to these oxides were observed, diffraction peaks assigned to the tetragonal phase showed no remarkable change after coloration with these liquids. In other words, coloration with Fe and Co ions does not appear to affect the crystalline phase or mechanical properties of the final product, as previously found [30]. Because ionic radii of  $Fe^{3+}$  and  $Co^{2+}$  are 0.0645 and 0.074 nm, respectively [29], both ions have little effect on the strain of the lattice, even if they substitute the  $Zr^{4+}$  site.

## 5. Conclusion

Pre-sintered blocks of three kinds of Y-TZP and one Ce-TZP/alumina nanocomposite were stained with six kinds of coloring liquid. The coloring effects of ivory liquid (containing Fe ions) on the three kinds of Y-TZP were greater than those on P-NANOZR because the translucency of these Y-TZPs was higher than that of P-NANOZR. When all the zirconia were

colored with liquid containing Er and Nd ions, cubic zirconia formed due to the stabilization by these elements, resulting in the reduction of flexural strength and fracture toughness. The three ivory liquids (containing Fe ions) and two violet liquids (containing Co ions) did not change the flexural strength and fracture toughness.

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