

Crystallographic and morphological analysis of sandblasted highly translucent dental zirconia

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SHORT TITLE: crystallography of sandblasted highly-translucent zirconia

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ABSTRACT

Objectives: To assess the influence of alumina sandblasting on four highly translucent dental zirconia grades. *Methods:* Fully sintered zirconia disk-shaped specimens (15-mm diameter; 0.5-mm thickness) of four highly translucent yttria partially stabilized zirconia (Y-PSZ) grades (KATANA HT, KATANA STML, KATANA UTML, Kuraray Noritake; Zpex Smile, Tosoh) were sandblasted with 50- μm alumina (Al_2O_3) sand (Danville) or left 'as-sintered' (control) (n=5). For each zirconia grade, the translucency was measured using a colorimeter. Surface roughness was assessed using 3D confocal laser microscopy, upon which the zirconia grades were statistically compared for surface roughness using a Kruskal-Wallis test (n=10). X-ray diffraction (XRD) with Rietveld analysis was used to assess the zirconia-phase composition. Micro-Raman spectroscopy was used to assess the potentially induced residual stress. *Results:* The translucency of KATANA UTML was the highest (36.7 ± 1.8), whereas that of KATANA HT was the lowest (29.5 ± 0.9). The ' Al_2O_3 -sandblasted' and 'as-sintered' zirconia revealed comparable surface-roughness S_a values. Regarding zirconia-phase composition, XRD with Rietveld analysis revealed that the 'as-sintered' KATANA UTML contained the highest amount of cubic zirconia ($c\text{-ZrO}_2$) phase (71 wt%), while KATANA HT had the lowest amount of $c\text{-ZrO}_2$ phase (41 wt%). KATANA STML and Zpex Smile had a comparable zirconia-phase composition (60 wt% $c\text{-ZrO}_2$ phase). After Al_2O_3 -sandblasting, a significant amount (over 25 wt%) of rhombohedral zirconia ($r\text{-ZrO}_2$) phase was detected for all highly translucent zirconia grades. *Significance:* Al_2O_3 -sandblasting did not affect the surface roughness of the three highly translucent Y-PSZ zirconia grades, but it changed its phase composition.

KEY WORDS: zirconia, alumina sandblasting, stress, XRD, micro-Raman

INTRODUCTION

Zirconia-based restorations are now frequently applied in dentistry, thanks to their esthetics, biocompatible properties, easier and even cheaper fabrication as compared to the conventional porcelain-fused-to-metal (PFM) restorations. [1, 2] Since 2014, more esthetic highly-translucent zirconia has been introduced into dentistry. According to Makhija *et al.*, full-contour restorations made by highly translucent zirconia are becoming the first choice to restore posterior teeth in the US. [3]

Interestingly, the phase composition of the highly translucent zirconia is different from that of conventional yttria-stabilized tetragonal zirconia polycrystals (Y-TZP). Due to a higher Y_2O_3 -stabiliser content (up to 9.42 wt% as compared to approximately 5.15 wt% for conventional zirconia, both according to the product information of zirconia powder from Tosoh), this highly translucent zirconia contains a significant amount of cubic zirconia ($c-ZrO_2$) phase and lower amount of alumina (Al_2O_3), rendering this zirconia more translucent. Moreover, such highly translucent zirconia ceramics are hydrothermally stable, because $c-ZrO_2$ grains do not transform to the monoclinic zirconia ($m-ZrO_2$) phase. A large amount of $c-ZrO_2$, on the other hand, results in a decrease in mechanical properties, especially in terms of strength and fracture toughness.

In order to adhesively lute zirconia-based restorations, specific pre-treatments are necessary to improve the surface properties and bonding receptiveness. According to a recent meta-analysis on the bonding effectiveness to zirconia ceramics, the combined mechanical and chemical surface pre-treatment of the zirconia surface was found essential to achieve durable bonding to zirconia. [4] Because zirconia ceramics exhibit stress-induced transformation, sandblasting will transform the surface structure, i.e. constrain as well as damage, which may influence its long-term performance. [5, 6] At the moment, however, only few papers reported on the influence of surface treatments on highly translucent zirconia. [7-9] The objective of this study was therefore (1) to investigate the

translucency and crystallographic characteristics of four highly translucent zirconia grades and (2) to assess the influence of Al₂O₃ sandblasting on the same four highly translucent dental zirconia grades. The null hypotheses tested were (1) that there is no difference in translucency and crystallographic characteristics among the four highly translucent zirconia grades and (2) that Al₂O₃ sandblasting does not affect the surface and crystallographic properties of highly translucent dental zirconia.

MATERIALS AND METHODS

The study design is schematically explained in Fig. 1. A summary of the characteristics and properties of the investigated highly translucent zirconia is provided in Table 1. Fully sintered zirconia disk-shaped specimens (15-mm diameter; 0.5-mm thickness) of four highly translucent yttria partially stabilized zirconia (Y-PSZ) grades (KATANA HT, KATANA STML, KATANA UTML, all Kuraray Noritake, Tokyo, Japan; Zpex Smile, Tosoh, Tokyo, Japan) were provided by the manufacturer, Kuraray Noritake (Table 1). One side of the specimens was ground and mirror polished to obtain the standardized thickness. All specimens were obtained in the form of sintered disks from the supplier and all surface treatments were directly applied to the pristine “as-sintered” side, which was not ground, nor polished during specimen preparation. The specimens were ultrasonically cleaned in acetone for 10 min and thoroughly dried with compressed air. All specimens of each grade were assigned into two groups of four specimens each and either were kept as-sintered (untreated) or sandblasted with 50- μ m Al₂O₃ sand (Danville, Danville, CA, USA) at 0.2 MPa for 15 s/cm² at a distance of 10 mm using a sandblasting device (Jet Blast II, Morita, Tokyo, Japan). Only the top surface received the surface treatment.

For each zirconia grade, the color and spectral reflectance were measured using a colorimeter (CR-13; Konica-Minolta Sensing, Tokyo, Japan). In this procedure, only the as-sintered specimens (n=5) from each zirconia grade were measured over a black (CIE $L^* = 28.4$, $a^* = -1.1$ and $b^* = -0.1$)

and a white (CIE $L^* = 94.1$, $a^* = -0.4$ and $b^* = 1.1$) background using a coupling medium (glycerin) applied between the zirconia specimens and the white and black background boards. [10] The as-sintered and mirror polished surface was used as the top- and backside, respectively. The translucency was obtained by calculating the color difference between the specimen with a white and black background: $TP = [(L_B - L_W)^2 + (a_B - a_W)^2 + (b_B - b_W)^2]^{1/2}$, where the subscripts refer to the color coordinates with, respectively, the black (B) and white (W) background. [11] The translucency was statistically compared for the four zirconia grades using one-way ANOVA followed by Tukey post hoc test.

One specimen from each zirconia grade was used for microstructural investigation using scanning electron microscopy (SEM, JSM-6701F, JEOL, Japan). After coating with a thin layer of osmium (Neo Osmium Coater, Meiwafoysis, Tokyo, Japan), secondary electron SEM images were acquired in vacuum (10^{-5} mbar), an acceleration voltage of 10 kV and a beam current of 144 μ A. The applied magnification was x10,000 for the as-sintered zirconia, and x3,000 for the Al_2O_3 sandblasted zirconia, respectively. The average grain size of the as-sintered specimens for each zirconia grade was measured according to the linear intercept method using the software Fiji (National Institutes of Health, Bethesda, MD, USA).

For the surface-roughness measurement, 20 specimens of each grade were prepared. Among 20 specimens, 10 specimens were left as-sintered, the other 10 were sandblasted with 50- μ m Al_2O_3 sand following the abovementioned conditions. Surface roughness was measured on the prepared specimens of each grade using a three-dimensional (3D) confocal laser microscopy (LEXT OLS4100, Olympus, Tokyo, Japan) at 100x magnification. Quantification of the 3D surface roughness parameter S_a (arithmetic mean deviation) was performed using LEXT software (Olympus). For each specimen, three regions (effective field of view was 128 μ m) on the surface-treated sides were selected. For surface roughness, the zirconia grades were statistically compared for surface roughness using a Kruskal-Wallis test.

Cu K α (40 kV, 40 mA) X-ray diffraction (XRD, D8 Advance, Bruker, Ettlingen, Germany) analysis was used for phase identification and calculation of the relative phase content of *c*-ZrO $_2$, *t*-ZrO $_2$ and *m*-ZrO $_2$ for both the as-sintered (control) and the Al $_2$ O $_3$ sandblasted specimens. The top surface of each specimen was analyzed from 20 to 90° 2 θ with a step size of 0.02° for 2 s. Rietveld analysis was used to assess the zirconia-phase composition using TOPAS academic V5 software (Coelho software, Brisbane, Australia). Based on the yttria-zirconia (Y $_2$ O $_3$ -ZrO $_2$) phase diagram, the sintering temperature and the *t*- and *c*-ZrO $_2$ contents from the Rietveld analysis, the overall Y $_2$ O $_3$ content in the highly translucent zirconia grades was estimated. Although equilibrium conditions were not reached under the applied sintering conditions, since the diffusion of yttrium is known to be very slow, the phase diagram and derived calculations at least reflect the relative phase content and their composition, allowing to compare the different material grades.

Micro-Raman spectroscopy (μ Raman) was performed in order to detect potential residual stresses on the surface. [12] Raman spectra (LabRAM HR Evolution, Horiba Scientific, Kyoto, Japan) were collected using the following conditions: Ar-ion laser with a wavelength of 532 nm, 10 mW power at sample and 100x objective. The spectrum integration time was 10 s with the recorded spectra averaged over two successive measurements. For each specimen, at least 25 measurements were performed using a pinhole aperture of 49.98 μ m. The Raman wavenumber of the *t*-ZrO $_2$ band around 146 cm $^{-1}$ was fitted and traced using LabSpec 6 software (Horiba Scientific).

All statistical tests were performed at a significance level of $\alpha=0.05$ using a software package R3.0 (R Foundation for Statistical Computing, Vienna, Austria) and a custom-made script for this software. Additionally, the degree of correlation between the translucency and the fraction of *c*-ZrO $_2$ phase was calculated for each grade using the abovementioned statistical software.

RESULTS

Fig. 2 summarizes the results of the translucency measurements. The translucency of KATANA UTML (Kuraray Noritake) was statistically significantly the highest (36.7 ± 1.8), whereas that of KATANA HT (Kuraray Noritake) was the lowest (29.5 ± 0.9). The translucency of KATANA STML (Kuraray Noritake) and Zpex Smile (Tosoh) was comparable and statistically not significantly different.

The results of the microstructural analysis using SEM are shown in Fig. 3. A number of large zirconia grains ($\geq 3 \mu\text{m}$) were observed for KATANA UTML (Kuraray Noritake). The average grain size of KATANA UTML (Kuraray Noritake) was the largest ($1.71\pm 0.36 \mu\text{m}$), whereas that of KATANA HT (Kuraray Noritake) was the smallest ($0.55\pm 0.92 \mu\text{m}$). The average grain size of KATANA STML (Kuraray Noritake) and Zpex Smile (Tosoh) were $1.11\pm 0.34 \mu\text{m}$ and $0.68\pm 0.13 \mu\text{m}$, respectively. After Al_2O_3 sandblasting, on the other hand, all highly translucent zirconia grades showed similar morphological characteristics.

The S_a surface roughness data are summarized in Fig. 4. Although Al_2O_3 sandblasted zirconia showed a slightly higher S_a , both as-sintered (control) and sandblasted specimens showed comparable S_a values for the three zirconia grades (KATANA STML, KATANA HT, and Zpex Smile). The Kruskal-Wallis test did not reveal a statistical difference in surface roughness among the as-sintered (control) and Al_2O_3 sandblasted zirconia for the three zirconia grades (KATANA STML, KATANA HT, and Zpex Smile), whereas Al_2O_3 sandblasted KATANA UTML showed a significantly higher roughness as compared to the as-sintered condition.

Regarding zirconia-phase composition, representative XRD patterns for each highly translucent zirconia grade are shown in Fig. 5. In addition, the Rietveld data are detailed in Table 2. XRD with Rietveld analysis revealed that for the 'as-sintered' specimens KATANA UTML (Kuraray Noritake) contained the highest amount of cubic zirconia ($c\text{-ZrO}_2$) phase (71 wt%), whereas KATANA HT (Kuraray Noritake) contained the lowest amount of $c\text{-ZrO}_2$ phase (41 wt%). KATANA STML (Kuraray

Noritake) and Zpex Smile (Tosoh) showed a comparable zirconia-phase composition (about 60 wt% *c*-ZrO₂) for the 'as-sintered' condition. These results are all in line with their mutually comparable translucency. The Y₂O₃ content for KATANA UTML (Kuraray Noritake) was the highest (5.4 mol%), whereas that for KATANA HT (Kuraray Noritake) was the lowest (4.0 mol%). Correlation analysis revealed that a larger amount of *c*-ZrO₂ fraction increased the translucency of highly translucent zirconia grades (Fig. 6). Calculated *R*² value was 0.98 (*p* = 0.0078). After Al₂O₃ sandblasting, a significant amount (over 25 wt%) of rhombohedral zirconia (*r*-ZrO₂) phase was detected for all highly translucent zirconia grades.

Representative μ Raman spectra and graphs revealing the *t*-ZrO₂ peak shifts for the highly translucent zirconia grades are shown in Fig 7. A clear peak shift of *t*-ZrO₂ band at 146 cm⁻¹ towards a higher wavenumber, implying the presence of a high compressive stress, was detected in each spectrum of the Al₂O₃ sandblasted specimens for all zirconia grades investigated. μ Raman detected *m*-ZrO₂ peaks for as-sintered and slightly less intensively for Al₂O₃ sandblasted KATANA HT (Kuraray Noritake). The shape of the spectra for as-sintered and Al₂O₃ sandblasted KATANA HT (Kuraray Noritake) was clearly different from those of the other three highly translucent zirconia grades.

DISCUSSION

The present study investigated the difference in translucency and crystallography of four highly translucent zirconia grades and the influence of Al₂O₃ sandblasting on the surface topography and crystallography of the highly translucent dental zirconia. Translucency measurement and crystallographic characterization revealed that the four highly translucent zirconia grades significantly differed, except for KATANA STML (Kuraray Noritake) and Zpex Smile (Tosoh), for which very similar data were recorded. Therefore, the first null hypothesis was rejected. For all the highly translucent zirconia grades (KATANA UTML, STML, HT, Kuraray Noritake; Zpex Smile, Tosoh), Al₂O₃

sandblasting resulted in a comparable surface roughness, but a substantially higher amount of *r*-ZrO₂ phase. Thus, the second null hypothesis that sandblasting does not affect the surface and crystallographic properties of highly translucent dental zirconia should be partially rejected.

To assess the translucency, a colorimeter was employed. According to previous reports, the translucency of 0.5-mm thick highly translucent zirconia ranged from 20 to 30. [13, 14] Our results showed higher TP values as compared to the previous reports. The difference can be caused by the choice of the coupling medium used for the TP measurement. Nogueira *et al.* reported a higher TP of glass ceramics when measured with glycerin as a coupling medium. [10] During the pilot test, we measured TP without coupling medium (glycerin), which resulted in a lower TP for all highly translucent zirconia grades investigated. Moreover, the translucency of highly translucent zirconia is correlated to the thickness of the specimens. [13] Our results revealed a clear and significant ($R^2=0.98$, $p=0.0078$) correlation between translucency and the amount of *c*-ZrO₂ phase. This result can be attributed to the fact that the *c*-ZrO₂ phase is more translucent than the *t*-ZrO₂ phase thanks to its isotropic crystal structure.

The SEM microstructural analysis revealed that the zirconia grain size of the 'as-sintered' highly translucent zirconia grades was differently distributed. In particular, KATANA UTML (Kuraray Noritake) showed a great number of large zirconia grains. According to the Rietveld analysis, KATANA UTML (Kuraray Noritake) contained the highest amount of *c*-ZrO₂. In general, the *c*-ZrO₂ grain size is larger than that of *t*-ZrO₂. [15] Moreover, the sintering temperature is known to affect the zirconia grain size. [16] In the present study, the sintering temperature of KATANA UTML and STML was 1550 °C, whereas that of KATANA HT (Kuraray Noritake) and Zpex Smile (Tosoh) was 1500 °C and 1450 °C, respectively. The grain-size distribution is mainly determined by the sintering temperature. A higher sintering temperature results in a larger grain size. [16] Although KATANA HT was sintered at higher temperature (1500 °C) than Zpex Smile (1450 °C), the average grain size of KATANA HT (Kuraray Noritake) was smaller than that of Zpex Smile (Tosoh). This must be related to the

difference in Y_2O_3 content. According to the Rietveld refinement, the estimated Y_2O_3 content of KATANA HT is 4.0 mol%, whereas that of Zpex Smile is 4.8 mol%. A higher Y_2O_3 content contributes to a higher amount of $c-ZrO_2$ and concomitant larger grain size.

Regarding surface-roughness measurement, two measurement options exist: a contact method versus a non-contact (optical) method. The contact method makes use of an instrument which records the vertical movements of a stylus displaced across the surface to be measured. Non-contact (optical) methods are based on microscopy imaging and faster than the aforementioned contact method. In this study, we used a confocal laser microscope as a non-contact (optical) method to measure S_a surface roughness. The advantages of confocal laser microscopy are: the ability to measure a smaller roughness than contact measurement tools; short measurement time; simultaneous observation of surface image and height profile; ability to obtain high-definition, fully-focused images that compete those of SEMs. [17] The disadvantage is, on the other hand, a limitation in the measurement target size. The resolution and the measuring area of the confocal laser microscope appeared however sufficiently high and adequate to assess the surface roughness of the highly translucent zirconia grades investigated.

We investigated the phase composition of the highly translucent zirconia grades using XRD. The highly translucent zirconia contained a significant amount of $c-ZrO_2$ phase, having improved their translucency. To identify the detailed zirconia-phase composition, several papers applied a Rietveld refinement. [14, 16, 18-20] Using the Rietveld refinement, the amount of zirconia phase can be calculated using the whole X-ray diffraction pattern and so reveal more precise data. Rietveld refinement revealed that Zpex Smile (Tosoh) contained 41.9 wt% $t-ZrO_2$ phase and 57.6 wt% $c-ZrO_2$ phase. This result was in line with the previous report by Zhang *et al.*. [14] For KATANA UTML, KATANA STML (Kuraray Noritake) and Zpex Smile (Tosoh), a broader peak with a shoulder was observed around $35^\circ 2\theta$. For KATANA HT, on the other hand, three clearly separated peaks were observed. This difference should be attributed to the difference in $c-ZrO_2$ content. The former three

highly translucent zirconia grades contained a relatively high amount of $c\text{-ZrO}_2$, which resulted in one broad peak composed of $t\text{-ZrO}_2$ (002), $c\text{-ZrO}_2$ (200) and $t\text{-ZrO}_2$ (110) peaks. KATANA HT (Kuraray Noritake) contained less $c\text{-ZrO}_2$, which led to three clearly separated peaks corresponding to $t\text{-ZrO}_2$ (002), $c\text{-ZrO}_2$ (200) and $t\text{-ZrO}_2$ (110). The $c\text{-ZrO}_2$ peak is positioned in between the $t\text{-ZrO}_2$ peaks. Hallman *et al.* reported these three separated peaks around $35^\circ 2\theta$ for KATANA HT (Kuraray Noritake). [21, 22] Their results are in agreement with our XRD patterns. Moreover, in the present study, the Y_2O_3 content of the highly translucent zirconia was estimated using the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ phase diagram reported by Scott. [23] The highest Y_2O_3 content was obtained for KATANA UTML (5.3 mol%), as deduced from the amount of $t\text{-}$ and $c\text{-ZrO}_2$ calculated by Rietveld refinement. According to our previous study [16], on the other hand, the Y_2O_3 content of the $t\text{-ZrO}_2$ phase of the conventional Y-TZP zirconia grades was 2.7 mol%. The higher amount of Y_2O_3 in the $t\text{-ZrO}_2$ phase resulted in a low transformability. This also contributed to the higher aging resistance of $t\text{-ZrO}_2$. Applied to this study, the highly translucent zirconia grades may have a higher aging resistance than the conventional Y-TZP zirconia grades. Further studies are needed to investigate this hypothesis.

For all highly translucent zirconia grades, sandblasted zirconia showed a broadened $t\text{-ZrO}_2$ (101) peak. The broadened $t\text{-ZrO}_2$ peak in 3 mol% yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) was reported in several papers particularly after surface treatment, for instance grinding or sandblasting. [6, 24-26] Hallmann *et al.* also reported the broadened tetragonal peak for highly translucent KATANA HT zirconia grades. [21] This broadened peak implies the presence of rhombohedral ZrO_2 ($r\text{-ZrO}_2$) phase [27, 28] or a distorted tetragonal zirconia. [29] We assume that this peak broadening resulted from $r\text{-ZrO}_2$ and calculated the phase composition by Rietveld refinement. The highly translucent zirconia contains a higher amount of yttria to improve their translucency. Most of the highly translucent zirconia investigated in the present study were 5 mol% Y_2O_3 stabilized zirconia. Kitano *et al.* reported the presence of $r\text{-ZrO}_2$ on 5 mol% Y_2O_3 stabilized zirconia after grinding. [30] They also reported that the rhombohedral phase was formed from both

the cubic and tetragonal phase in fully and partially stabilized zirconia. In addition, we have prepared cubic zirconia phase specimens (prepared from TZ-8Y Tosoh powder and composed of 100% *c*-ZrO₂ after sintering) in order to evaluate the crystallographic change to cubic zirconia after sandblasting. TZ-8Y Tosoh powder was subjected to uniaxial pressing and sintered at 1450 °C. Three TZ-8Y specimens were prepared. One side of the specimens was Al₂O₃ sandblasted following the abovementioned conditions, whereas the other specimen side was left as sintered. Both specimen sides were analyzed by XRD from 20 to 90° 2θ with a step size of 0.02° for 2 s. Al₂O₃ sandblasted TZ-8Y (Tosoh) showed broadened peaks around 30°, 50° and 60° 2θ (closed black arrows in Fig. 8), which indicates the presence of *r*-ZrO₂ phase. Rietveld refinement revealed that the as-sintered TZ-8Y specimens contained 99.8 wt% *c*-ZrO₂, whereas the surface of Al₂O₃ sandblasted TZ-8Y was composed of 69 wt% *c*-ZrO₂ and 31 wt% of *r*-ZrO₂. Besides this *r*-ZrO₂ peak around 29.7° 2θ (open white arrows in Fig. 5b), additional *r*-ZrO₂ peaks were observed around 49.5° and 58.7° 2θ (closed black arrows in Fig. 5b), which is in agreement with the JCPDF (Joint Committee on Powder Diffraction File) file No. 01-083-1850. Rietveld refinement confirmed the presence of a significant amount of *r*-ZrO₂ phase for all four highly translucent zirconia grades investigated.

The Katana HT ceramic also shows a small XRD peak around 28° 2-θ after sintering and especially after sandblasting, which reflects a small amount of monoclinic ZrO₂ phase (see Fig. 5). The amount of *m*-ZrO₂ after sandblasting, as well as in the as-sintered condition, was also determined by means of Rietveld analysis to be the highest for this grade (see Table 2). This was confirmed by the Raman spectra presented in Fig. 7.

We used μRaman to analyze the residual surface stress of highly translucent zirconia grades. μRaman analysis revealed comparable spectra for the three highly translucent zirconia grades KATANA UTML, KATANA STML and Zpex Smile. KATANA HT (Kuraray Noritake) showed a clearly different μRaman spectrum, indicating the presence of different phases or additives as compared to the other three highly translucent zirconia grades. However, the μRaman spectra reported by

Hallman *et al.* were also different from ours. Further analysis is needed to identify those differences. [22] Regarding residual stress analysis, Pezzotti and Porporati reported that μ Raman peaks linearly shifted corresponding to the presence of residual stresses. [12] Previously, we reported the presence of the residual compressive stress on surface-treated (sandblasted, rough polished and ground) conventional Y-TZP zirconia. [6, 31] In this study, we detected a clear t -ZrO₂ peak shift towards a higher wavenumber, indicating the presence of residual compressive stresses for all highly translucent zirconia investigated. Although the highly translucent zirconia grades contained various amounts of t -ZrO₂, all of them showed the presence of residual compressive stress. Further research is needed to calculate the actual residual stress values using a calibration method. [32]

According to the systematic reviews published recently, [4, 33] the combined mechanical and chemical pre-treatments are mandatory for durable bonding to zirconia. When we focus on mechanical pre-treatments, alumina sandblasting can be regarded as one of the most popular and effective surface treatments. However, surface treatments of highly translucent zirconia have not well been studied yet. In the present study, we focused solely on the morphological and crystallographical aspects of sandblasted highly-translucent zirconia grades. In the continuation of this work, it would be interesting to investigate the influence of surface treatment on the mechanical properties of highly translucent dental zirconia. In addition, low-temperature degradation (LTD) behavior of the highly translucent zirconia is not well studied yet. Therefore, the LTD behavior of surface-treated highly translucent zirconia could be of interest in future research.

CONCLUSION

Al₂O₃ sandblasting did not significantly increase surface roughness of the highly translucent Y-PSZ zirconia grades except for KATANA UTML (Kuraray Noritake). However, it changed the phase

composition and residual stress presence at the surface of all highly translucent zirconia grades investigated.

ACKNOWLEDGEMENTS

We would like to thank Kuraray Noritake for supplying zirconia disks. We acknowledge Ms. Tomoko Numata at *HORIBA TECHNO SERVICE (Tokyo, Japan)* for supporting the micro-Raman spectroscopy. This work was supported by the JPSP Grant-in-Aid for Scientific Research (C) 16K11622.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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FIGURE

Figure 1.

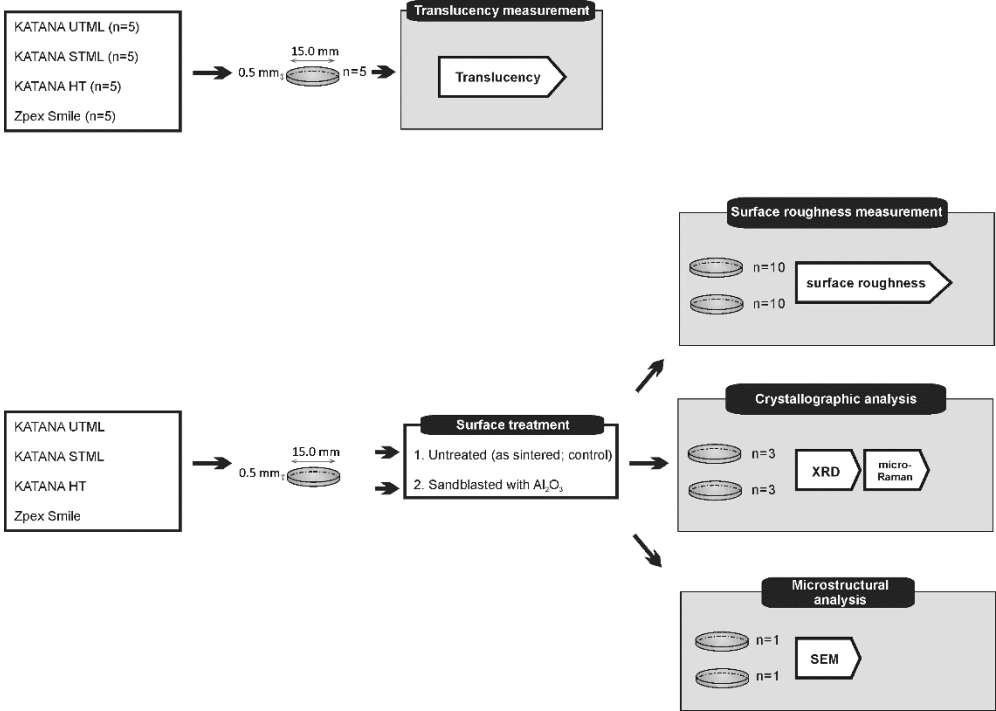


Figure 2.

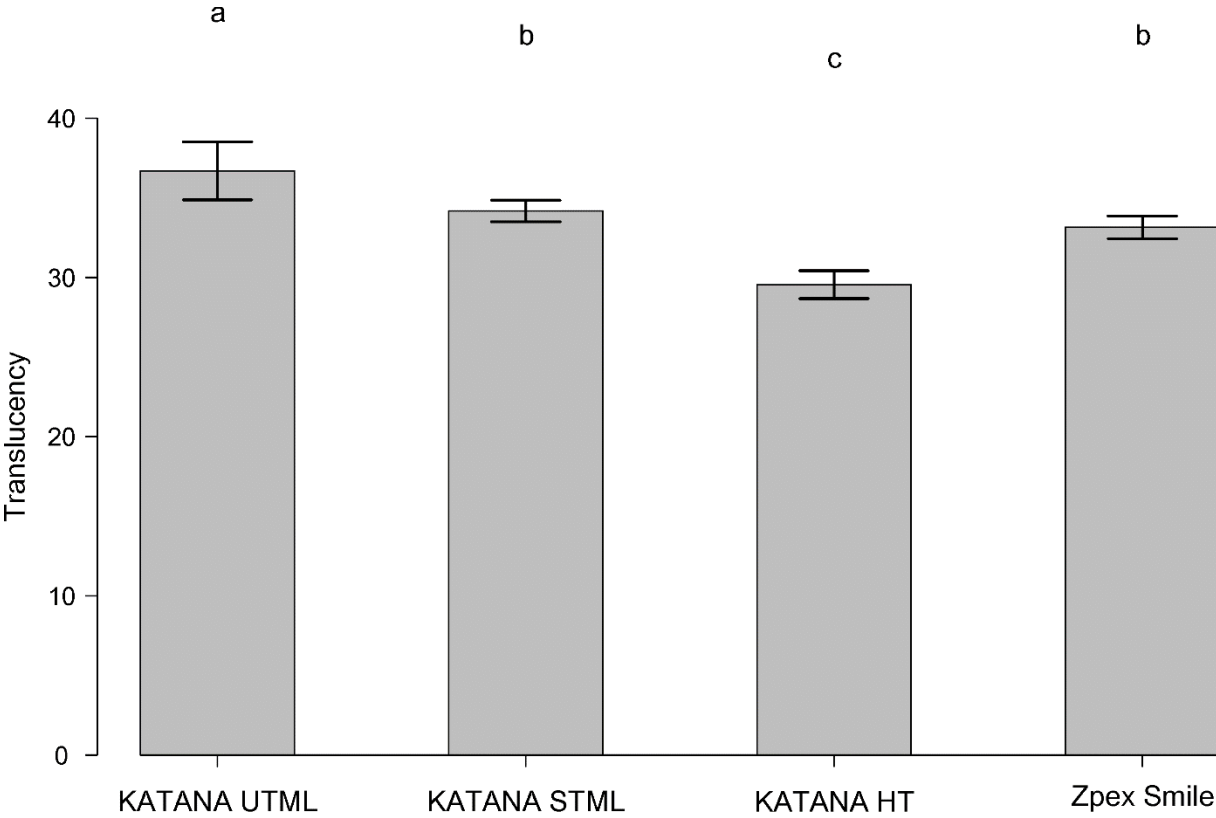


Figure 3.

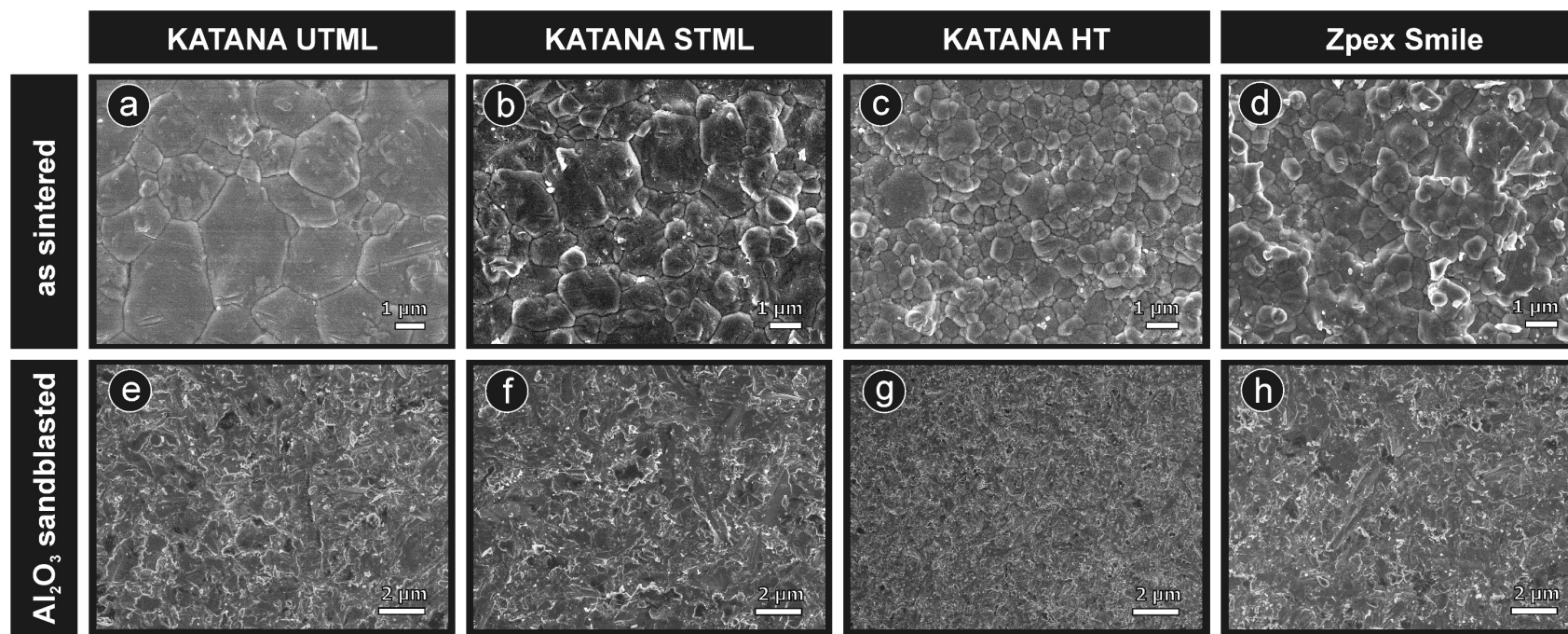


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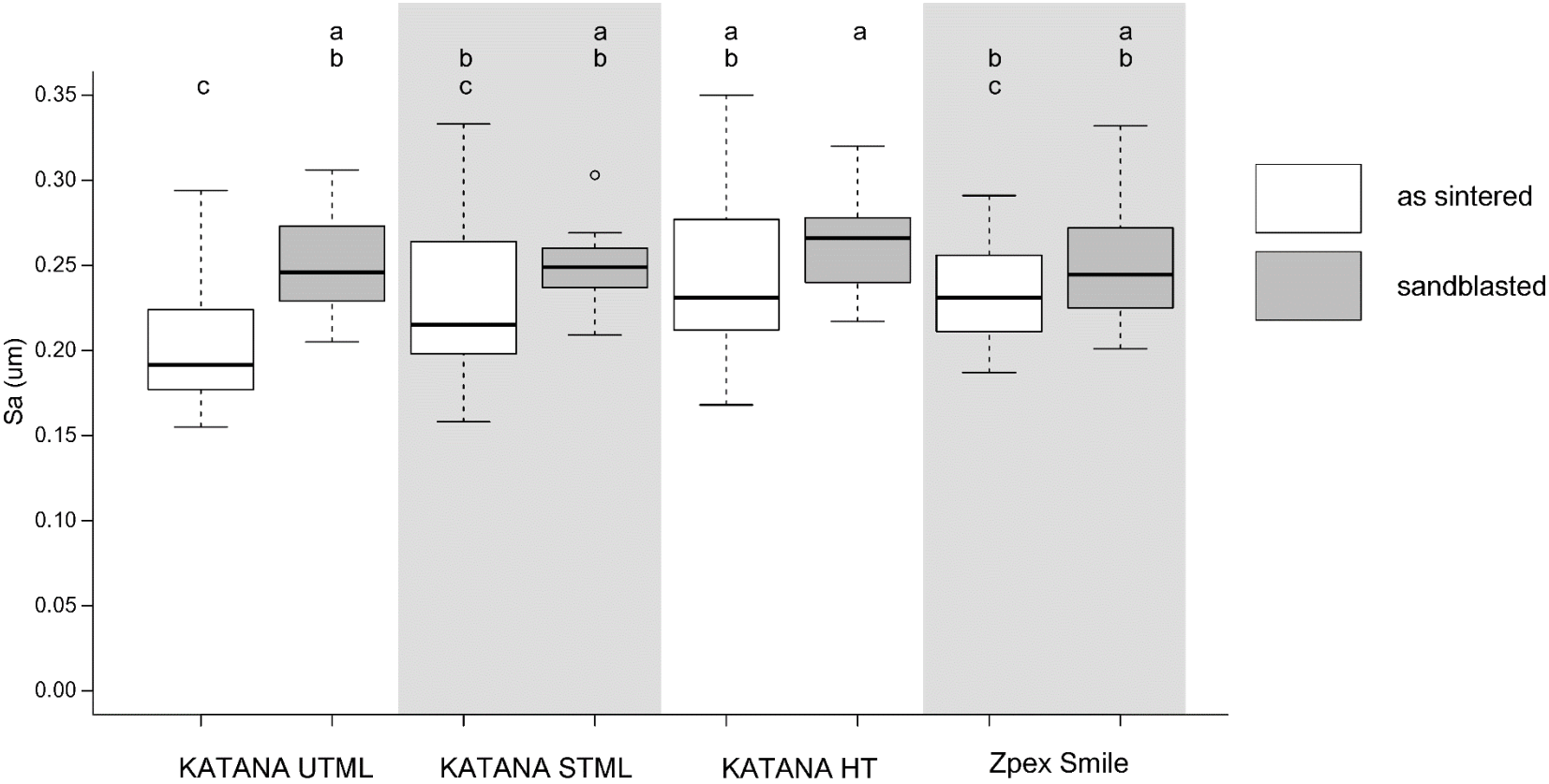


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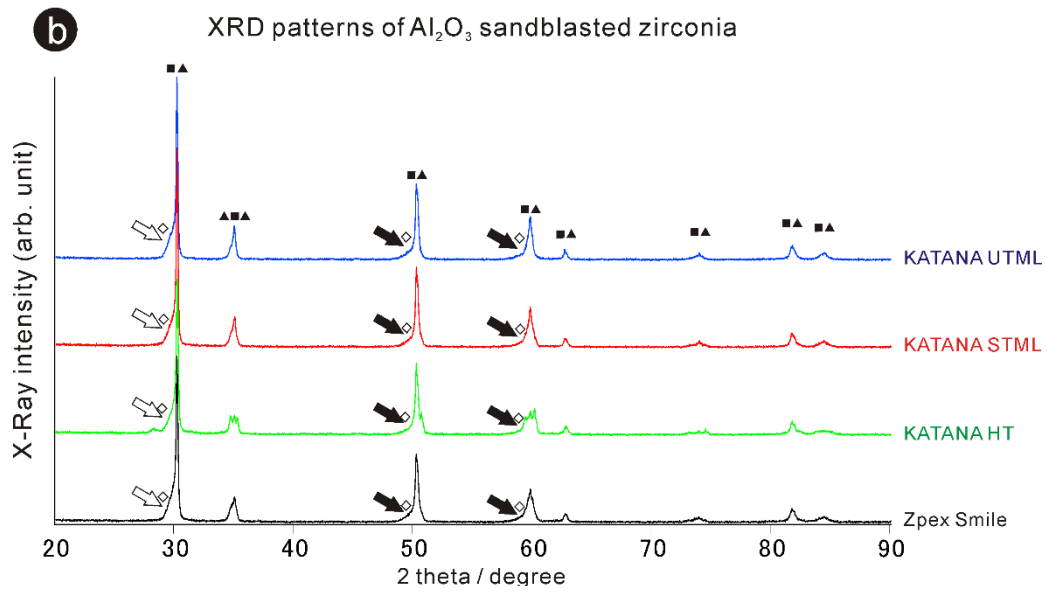
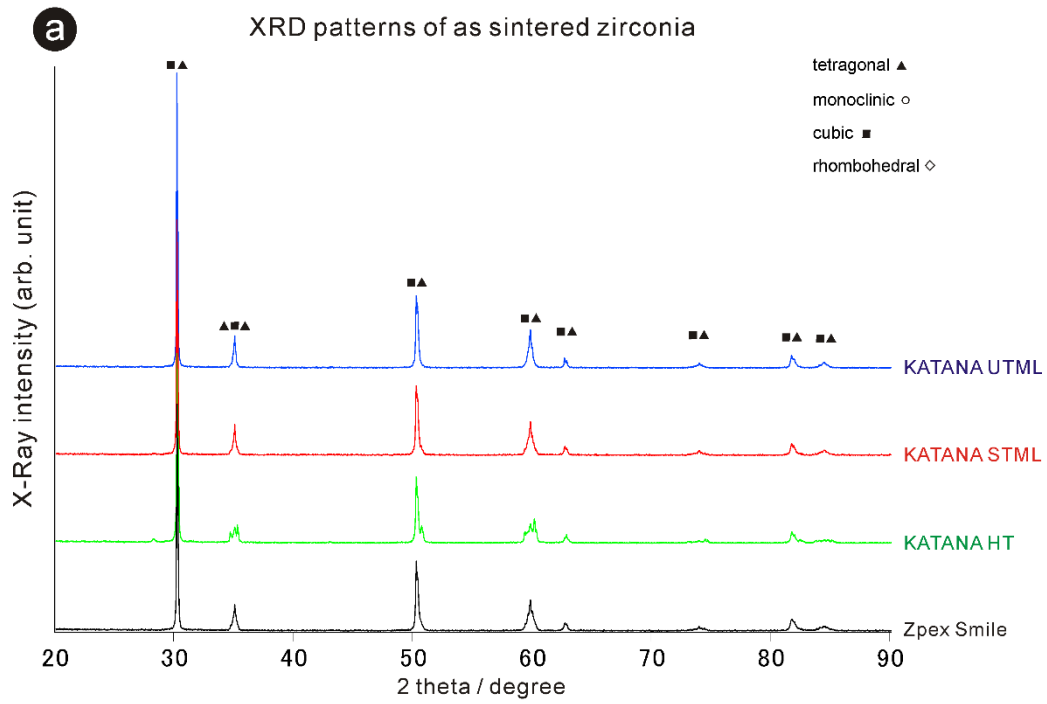


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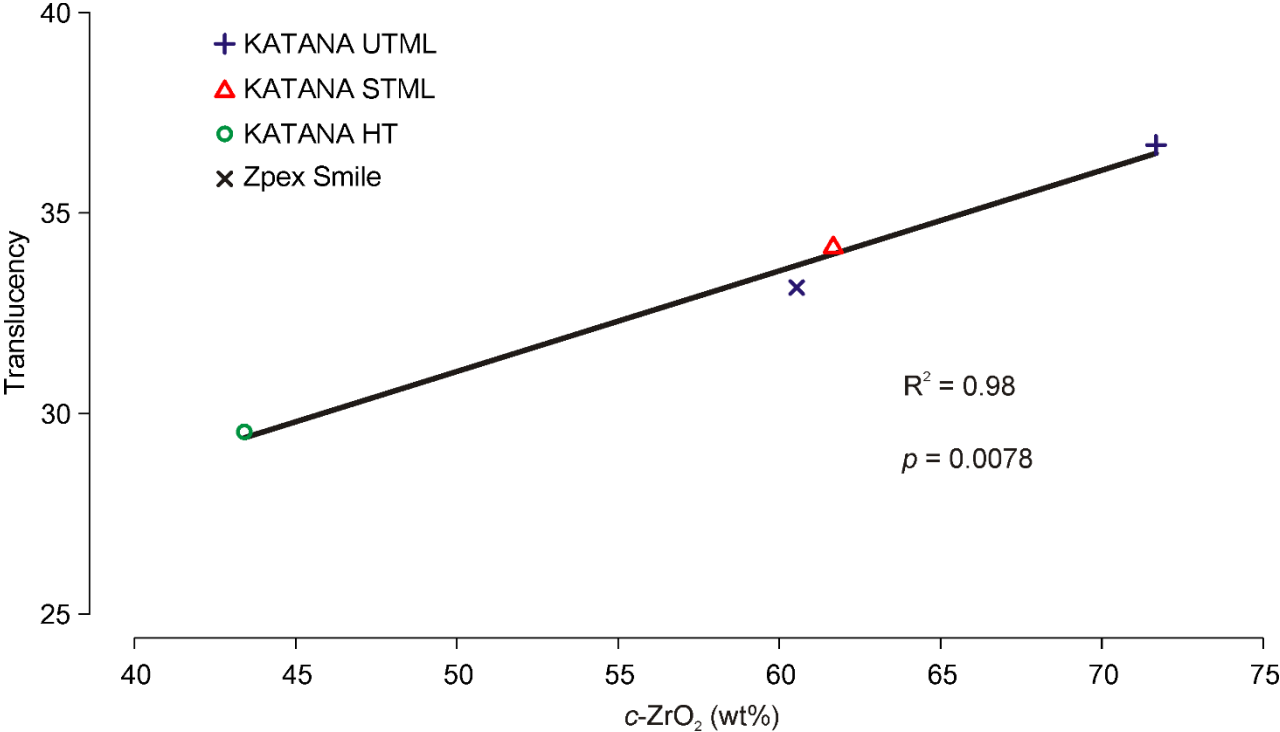


Figure 7.

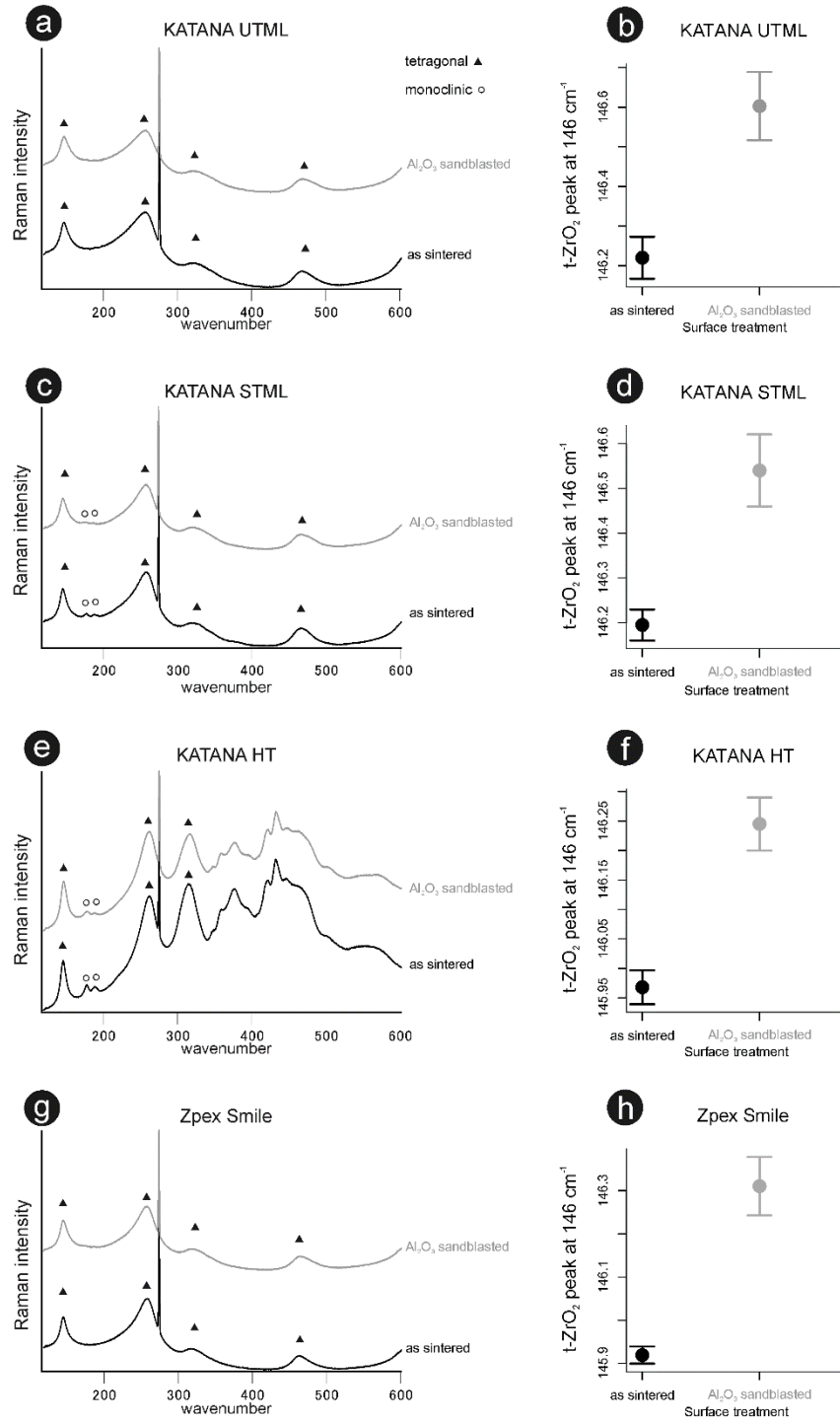
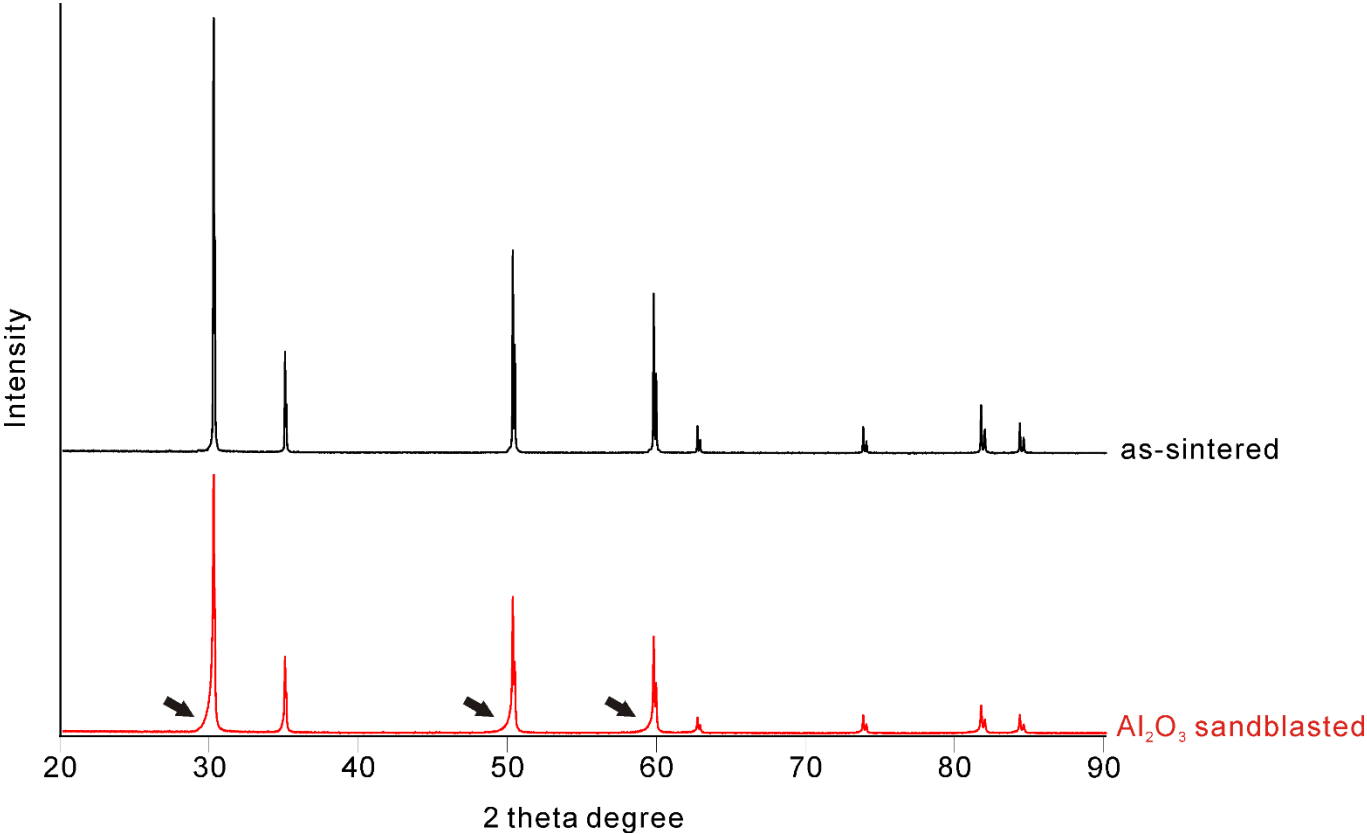


Figure 8.



TABLES

Table 1. Characteristics and properties of the highly translucent zirconia grades investigated.

Zirconia grade	Manufacturer	Lot	Sintering conditions		Flexural strength (MPa)*	Toughness (MPa m ^{1/2})*
			Temperature (°C)	Dwelling time (hrs)		
KATANA UTML	Kuraray Noritake	60W15C01	1550	2	500-600	2.2-2.7
KATANA STML	Kuraray Noritake	55W15C01	1550	2	600-800	2.5-3.5
KATANA HT	Kuraray Noritake	W215F06	1500	2	900-1100	3.5-4.5
Zpex Smile	Tosoh	XY554244G	1450	2	400-500	2.2-2.7

*: values reported by Zhang Y and Lawn BR. [34]

Table 2. Summary of the Rietveld analysis.

Zirconia grade	Surface condition	<i>c</i> -ZrO ₂ (wt%)	<i>t</i> -ZrO ₂ (wt%)	<i>m</i> -ZrO ₂ (wt%)	<i>r</i> -ZrO ₂ (wt%)	GoF ¹	Estimated Y ₂ O ₃ content (mol%)
KATANA UTML	as-sintered	70.6	28.9	0.2	0.3	2.09	5.4
	Al ₂ O ₃ sandblasted	50.7	13.8	1.0	30.2	1.72	
KATANA STML	as-sintered	59.9	39.5	0.4	0.2	1.99	4.8
	Al ₂ O ₃ sandblasted	47.6	18.4	1.9	32.1	1.69	
KATANA HT	as-sintered	41.7	57.3	0.8	0.2	1.63	4.0
	Al ₂ O ₃ sandblasted	36.6	32.3	4.5	26.7	1.62	
Zpex Smile	as-sintered	57.6	41.9	0.1	0.4	1.93	4.9
	Al ₂ O ₃ sandblasted	46.5	20.5	1.4	31.6	1.64	

¹GoF: goodness of fit in Rietveld analysis.

FIGURE LEGENDS

Figure 1. Flow chart detailing the study setup.

Figure 2. Graph presenting the translucency of the four highly translucent Y-PSZ grades investigated in bar plot (whisker: standard deviation). One-way ANOVA revealed that the highest translucency was recorded for KATANA UTML (36.7 ± 1.8), whereas that of KATANA HT was the lowest (29.5 ± 0.9). Translucency of KATANA STML (34.2 ± 0.7) and Zpex Smile (33.1 ± 0.7) were comparable and were statistically not different.

Figure 3. Representative SEM photomicrographs of the 'as-sintered' and ' Al_2O_3 sandblasted' zirconia for each highly translucent zirconia grade. **(a-d)** 'As-sintered' highly translucent zirconia grades. A number of large zirconia grains were observed for KATANA UTML (Kuraray Noritake), whereas KATANA HT contained both larger and smaller zirconia grains; KATANA STML resulted in a larger zirconia grain size than Zpex Smile. **(e-h)** ' Al_2O_3 sandblasted' highly translucent zirconia grades. Each highly translucent zirconia specimen showed a similar rough surface.

Figure 4. Graph presenting the Sa surface roughness of the four highly translucent Y-PSZ grades in boxplot (boxes: first quartile and third quartile; whiskers: largest value within 1.5 interquartile range from third quartile and minimum value; horizontal line: median). Although the sandblasted zirconia showed slightly higher Sa values, both the 'as-sintered' (control) and ' Al_2O_3 sandblasted' specimens showed statistically insignificant Sa values for zirconia grades except for KATANA UTML. The Kruskal-Wallis test revealed no statistical difference between the 'as-sintered' (control) and ' Al_2O_3 sandblasted' zirconia for all zirconia grades.

Figure 5. Representative XRD patterns of 'as-sintered' (control) zirconia **(a)** and of 'Al₂O₃ sandblasted' zirconia **(b)**. KATANA UTML showed clear *c*-ZrO₂ (200) peaks and small *t*-ZrO₂ (002), (110) peaks, whereas KATANA HT showed separated *c*-ZrO₂ (200) peak and *t*-ZrO₂ (002), (110) peaks. KATANA STML and Zpex Smile showed similar XRD patterns. In addition, 'Al₂O₃ sandblasted' zirconia showed a broadened (101) tetragonal peak (open white arrows in **(b)**) for all highly translucent zirconia grades, which implies the presence of rhombohedral ZrO₂ (*r*-ZrO₂) phase. Additional *r*-ZrO₂ peaks were observed around 49.5° and 58.7° 2θ (closed black arrows in **(b)**).

Figure 6. Correlation between amount of *c*-ZrO₂ and translucency. Correlation analysis revealed that a higher amount of *c*-ZrO₂ resulted in a higher translucency ($R^2=0.98$, $p=0.0078$).

Figure 7. Representative μ Raman spectra **(a, c, e, g)** and the 146 cm⁻¹ of *t*-ZrO₂ peaks shift graphs **(b, d, f, g)**: mean and 95% confidence interval) of the 'as-sintered' and 'Al₂O₃ sandblasted' highly translucent zirconia grades. Al₂O₃ sandblasting resulted in a clear peak shift toward a higher wavenumber for all highly translucent zirconia grades investigated. Note that the shape of the μ Raman spectra for KATANA HT was clearly different from those recorded for the other three highly translucent zirconia grades.

Figure 8. Representative XRD patterns of TZ-8Y (Tosoh) specimens. Al₂O₃ sandblasted TZ-8Y (Tosoh) showed broadened peaks around 30°, 50° and 60° 2θ (closed black arrows in Fig. 8), which indicates the presence of *r*-ZrO₂ phase. Rietveld refinement revealed that the as-sintered TZ-8Y (Tosoh) specimens contained 99.8 wt% *c*-ZrO₂, whereas the surface of Al₂O₃ sandblasted TZ-8Y (Tosoh) was composed of 69 wt% *c*-ZrO₂ and 31 wt% of *r*-ZrO₂.