Silicon nitride ceramic for all-ceramic dental restorations

Mahmut Sertaç ÖZDOĞAN, Mustafa GÜNGÖRMÜŞ, Ali ÇELİK and Gülsüm TOPATES

1 Department of Prosthodontics, Ankara Yıldırım Beyazıt University, Ankara, Turkey
2 Department of Biomedical Engineering, Ankara Yıldırım Beyazıt University, Ankara, Turkey
3 Department of Basic Sciences School of Dentistry, Ankara Yıldırım Beyazıt University, Ankara, Turkey
4 Department of Metallurgical and Materials Engineering, Bilecik Şeyh Edebali University, Bilecik, Turkey
5 Department of Metallurgical and Materials Engineering, Ankara Yıldırım Beyazıt University, Ankara, Turkey
Corresponding author, Mahmut Sertaç ÖZDOĞAN; E-mail: msozdogan@ybu.edu.tr

Silicon nitride (Si₃N₄) is one of the promising ceramics for dental restoration due to providing significant benefits during the application. This study aimed to investigate the potential use of Si₃N₄ for all-ceramic dental restorations by characterizing some critical properties as color shade, mechanical resistance, shear-bond strength and radiolucency. For our study, porous Si₃N₄ ceramic was produced by partial sintering process with limited amounts of sintering additives and low temperature. A commercial ZrO₂ ceramic was prepared according to manufacturer's instructions and results were compared with Si₃N₄. Si₃N₄ is an attractive ceramic for dental applications with good mechanical properties even in porous form, it has additional advantages over the conventional ceramics used as restorative material, such as, inherent antibacterial/anti-infective activity, radiolucency, and lower hardness. It is expected that Si₃N₄ will become popular in dental applications as well.

Keywords: Bioengineering, Biomaterial(s), Crowns, Dental materials, Ceramics

INTRODUCTION

In recent years, ceramic restorations without metal infrastructure have become more popular due to their superior aesthetics and biocompatibility. The development of high toughness and high strength ceramic materials with new techniques has attracted the attention of dentists, dental technicians and patients. The increased awareness of metal-free prosthesis restorations has led to the development of many ceramic restoration systems1-3.

Due to its good mechanical properties, ZrO₂ is widely used in medical and engineering fields4. Even though ZrO₂ provides many advantages in dental applications, it shows low temperature degradation (aging), which is aggravated in the presence of water. This degradation results in grain pullout, microcracking accompanying strength decreases5. Therefore, search for novel ceramic systems in the field of dentistry continues.

Si₃N₄ is an attractive ceramic restorative application. Due to its high wear resistance, proper fracture toughness and moderate elastic modulus, it has been adopted for biomedical applications, specifically for orthopedic joint implants6,7. Several studies have shown that, besides its good mechanical properties, Si₃N₄ is a biocompatible material for implant or prosthetic purposes8.9.

Another attractive attribute of Si₃N₄ as restorative material is its inherent radiolucency. An ideal restorative material is expected to have a high enough radiopacity to be able to be distinguished from the surrounding tissues and low enough radiopacity to allow detection of voids in the material and recurrent caries10. The most common synthetic dental ceramic, Yttria-stabilized tetragonal zirconia polycrystalline (Y-TZP), have the same radiopacity with metals used in dentistry, such as Cr-Ni alloy and gold11. The low radiopacity of Si₃N₄, on the other hand, allows for both the implant and the underlying bone to be imaged using plain radiography in orthopedic applications12.

Bacterial adhesion/colonization on restorative materials is an important factor determining the risk for secondary caries formation. One of the reasons Si₃N₄ is considered as a dental restorative/implant material is its inherent antimicrobial properties. The exact mechanism of Si₃N₄’s antimicrobial activity is still being investigated but several mechanisms have been proposed. Ultra-hydrophilic and strong negative charged Si₃N₄ surfaces are easily obtainable13. The ultra-hydrophilicity results in a highly ordered water structure close to the surface, which acts as a physical barrier against bacteria coming into direct contact with the surface14. The strong negative surface charge is also thought to contribute to the antimicrobial effect by resulting in an electrostatic repulsion between the also negatively charged bacterial membrane15. Another mechanism that has been shown to contribute to antimicrobial behavior is formation of peroxynitrite that is toxic for several bacteria types through oxidation process16-18.

Despite its opportune combination of properties, there is a limited number of studies on the potential of Si₃N₄ as a dental material. One of the main reasons is the improper color of Si₃N₄ ceramics for core/crown applications19. The color of Si₃N₄ ceramics are affected
by various factors, such as, type and oxidation state of the rare-earth additives, impurities, grain boundaries and porosity. Dense Si₃N₄ ceramics are considered too dark colored for especially restorative applications. However, lighter colors, suitable for dental applications, can be obtained when open porosity is introduced into Si₃N₄ ceramics²⁰.

This work aims to investigate some critical properties of Si₃N₄ for possible restorative applications. Si₃N₄ ceramic were produced via partial sintering, thus some amount of open porosity was formed within samples. Physical, mechanical, adhesive, optical and radiolucency properties of the produced ceramics were characterized and compared with a commercial ZrO₂ dental ceramic.

MATERIALS AND METHODS

Preparation of samples

1. Fabrication of Si₃N₄ samples

Si₃N₄ ceramics were prepared using α-Si₃N₄ powder (SN-E-10, Ube Industries, Yamaguchi, Japan) by adding 2.50 wt% Y₂O₃ (Grade C, H.C. Starck, Selb, Germany) and 2.50 wt% CeO₂ (Inframat, Manchester, CT, USA) as sintering additives. Uniaxial dry pressing was used for shaping the samples.

For three-point flexural test, bar-shaped samples were prepared according to ISO 14704:2000. For radiography and color shade measurement tests, disk-shaped samples with a diameter of 10 mm and 0.50, 1.00 and 1.50 mm thickness were prepared (n=10 for each thickness).

For shear bond strength (SBS) test, 5×5×5 mm cubic samples were prepared. All samples were sintered by pressureless sintering in a graphite furnace (FCT Anlagenbau, Germany) at 1,700°C for 1 h under N₂ atmosphere.

2. Fabrication of ZrO₂ samples

For radiography and color shade measurement tests, disk-shaped samples with a diameter of 10 mm and 0.50, 1.00 and 1.50 mm thickness were prepared (n=10 for each thickness).

For SBS test, 3×3×3 mm cubic specimens were prepared. All ZrO₂ samples were prepared from commercially available pre-sintered ZrO₂ discs (Zirking, Huge Dental, Shandong, China) using a CAD-CAM device (CAD; Dental Wings Open System, DWOS, Montréal, Canada, CAM: Yenadent D40 CAM, ZenoTec, Istanbul, Turkey). ZrO₂ specimens were sintered in a high-temperature furnace (Protherm MoS-B 150/1, Alser Teknik, Ankara, Turkey) for 2 h at 1,375°C.

Both Si₃N₄ and ZrO₂ samples were airborne-particle abraded with 50 μm Al₂O₃ particles (BEGO Korox, Bremen, Germany) applied perpendicular to the specimen surface at 0.28 MPa pressure, from 10 mm distance for 20 s. All specimens (except for Si₃N₄ bars) were polished using 800-grit silicon carbide (SiC) paper (Struers, Willich, Germany).

3. Physical and mechanical characterization of samples

Open porosity and bulk density values of samples were determined by Archimedes’ displacement method according to ASTM C-20 standards²¹. Pore size distribution was measured by mercury intrusion porosimetry (MIP) (Autopore IV, Micromeritics, Norcross, GA, USA).

X-ray diffraction (XRD) was performed for phase analysis using monochromatic Cu-Kα radiation (λ=1.5406 Å) (Rigaku MiniFlex-600, Tokyo, Japan). The microstructure was investigated by scanning electron microscopy (SEM) (Hitachi SU5000, Tokyo, Japan) from the fracture surface of samples.

Mechanical characterization of samples was done according to ASTM C1161-18 standards²². Using ten specimens with 3×4×50 mm dimensions, three-point flexural strength and elastic modulus measurements were done. Bending load was applied using a universal testing machine (Instron 5581, Backinghamshire, UK) at a cross-head speed of 0.5 mm/min with a support span of 40 mm. Due to the porosity of Si₃N₄ samples, no grinding and polishing steps were applied for bar specimens. Hardness measurements were performed by Vickers indenter (Shimadzu HMV-G, Kyoto, Japan) at load of 98 N for 10 s.

Color shade measurement

Color shade measurements were performed between 400–700 nm with a clinical spectrophotometer (VITA Easyshade V, VITA Zahnfabrik, Bad Säckingen, Germany) with a probe tip of 5 mm. Illumination of the specimen was provided by the LED light from the periphery of the tip into the specimen surface. The display of the spectrophotometer shows the closest VITA shade in the VITA Classical shade guide from A1 to D4. The samples were photographed with Vita Classical A1-D4 Shade Guide under naturel daylight.

Shear-bond strength measurement

The SBS measurements were done on extracted caries free third molars. The protocol was approved by the Ethics Committee of the Ankara Yıldırım Beyazıt University, under the protocol number 29.05.2019/40.

Twenty caries free third molars were collected at the Tepebasi Oral and Dental Health Hospital of Ankara Yıldırım Beyazıt University, Turkey. Collected teeth were kept in 0.5% Chloramine T (Explicit Chemicals, Pune, India) at 4°C until the time of use. The teeth were cut in mesiodistal direction just above the cementoenamel junction using a Micracut 201 automated precision cutting machine with water cooling (Metkon, Bursa, Turkey) to expose a flat dentin. The exposed dentin surfaces were visually investigated to ensure the absence of residual enamel and exposure of the pulp. Teeth with residual enamel were further ground down until flat dentin surfaces were achieved. Teeth with exposed pulp were not used. The teeth were then embedded in self-curving dental acrylic (IMICRYL Cold cure, Konya, Turkey) up to a few millimeters below the sectioned surface with the aid of a plastic mold.
The prepared specimens were randomly assigned into three groups ($n=10$ for each group). In group 1 Si$_3$N$_4$ cubes were first treated with a silane coupling agent (Ultradent, South Jordan, UT, USA) for 2 min and then luted to dentin. In group 2 and 3 Si$_3$N$_4$ and ZrO$_2$ cubes were luted to dentin directly, without pretreatment with a coupling agent. Panavia Cement SA Plus (Kuraray Noritake Dental, Tokyo, Japan) was used as adhesive in all groups. Each cube was luted under 1 kg fixed pressure and light-cured for 20 s from four sides (5 s×4 sides) using an LED lamp (Linuo, Yunnan, China) with a light output of not less than 800 mW/cm$^2$.

The cemented specimens were subjected to thermal cycling alternating between 5°C and 55°C for 72 h using an automated thermal cycler (THE-1100, SD Mechatronik, Feldkirchen-Westerham, Germany). Following the thermal cycling, shear strength measurements were performed using a universal testing machine (Lloyd LRX, Ametek, Berwyn, PA, USA). A force parallel to the sectioned surface was applied at the base of the cubes with 1 mm/min cross-head speed until fracture. One-way ANOVA ($\alpha=0.05$) was used for statistical analysis of the SBS measurements.

**Radiopacity measurement**

Disk shaped Si$_3$N$_4$ and ZrO$_2$ specimens with thickness values of 0.50, 1.00 and 1.50 mm ($n=10$ for each group) were prepared for radiopacity measurements. Each disk was numbered, and the thickness of each disk was determined using a digital caliper. The disks were then placed on a photostimulable phosphor (PSP) imaging plate (ScanX; Air Techniques, Melville, NY, USA). A 99% pure graduated aluminum step wedge, thickness ranging from 1 to 11 mm was also placed on the PSP imaging plate as control. Radiographs were taken using a dental X-ray unit (Villa Sistemi Medica, Buccinasco, Italy) maintaining the X-ray beam perpendicular to the specimens at 70 peak kilovoltage (kVp), 0.32 s exposure and 7 mA current. The radiographs were saved as TIFF files. The radiodensity (average pixel intensity) of the samples were determined using ImageJ software v1.52a (National Institute of Health, Bethesda, MD, USA) by selecting a region on the image and measuring the pixel intensity value. First the radiodensity of each step on the aluminum step wedge was measured. Then the intensity of each disk was measured and the thickness vs. radiodensity values were plotted for the Si$_3$N$_4$, ZrO$_2$ and Al specimens. Kruskal-Wallis and Tukey multiple comparison tests ($\alpha=0.05$) were used for statistical analysis.

**RESULTS**

**Densification and phase development of Si$_3$N$_4$ and ZrO$_2$ samples**

The porosity and pore characteristics of Si$_3$N$_4$ and ZrO$_2$ are listed in Table 1. Partial sintering (by using limited sintering additives and lower sintering temperature) enabled formation of porous Si$_3$N$_4$. Relative densities of Si$_3$N$_4$ and ZrO$_2$ were measured as 84.12 and 99.23%.

![Fig. 1](image-url)  
**Fig. 1** SEM images of the produced Si$_3$N$_4$ ceramic under (a) 5,000× and (b) 15,000× magnification and (c) XRD patterns of Si$_3$N$_4$ and ZrO$_2$ (β: β-Si$_3$N$_4$, Y: Y$_2$SiO$_4$, Z: t-ZrO$_2$).

| Property                | Si$_3$N$_4$       | ZrO$_2$        |
|-------------------------|-------------------|----------------|
| Bulk density (g/cm$^3$)  | 2.70±0.03         | 6.02±0.01      |
| Open porosity (%)       | 10.5±0.0          | 0.006±0.003    |
| Relative density (%)    | 84.12±0.01        | 99.20±0.00     |
| Average pore size (μm)  | 1.14              | —              |
| Flexural strength (MPa) | 418.1±71.2        | 582.3±72.3     |
| Elastic modulus (GPa)   | 157.5±5.4         | 174.5±13.5     |
| Hardness (HV10) (GPa)   | 10.9±0.4          | 13.7±0.4       |
respectively. The open porosity of Si₃N₄ was 10.54% where nearly no open porosity was measured for ZrO₂.

Rod-like β-Si₃N₄ grains with various thicknesses were developed in the structure as seen in Figs. 1a and b. The presence of porosity shows that the densification was successfully controlled by partial sintering. The micron-size pore was compatible with the size of pore that was measured by MIP. Also, strong neck formation was observed (Fig. 1b), that contributes to the mechanical resistance of the ceramic.

XRD analysis showed that the produced ceramic contains β-Si₃N₄ as the major phase and Y₂SiO₅ has been formed by the reaction between Y₂O₃ and SiO₂ (the passive oxide layer of Si₃N₄) as the secondary phase (Fig. 1c). t-ZrO₂ was detected as the only phase in ZrO₂ ceramic.

Mechanical characterization of Si₃N₄ and ZrO₂ ceramics

Flexural strength, elastic modulus and hardness values of Si₃N₄ and ZrO₂ are given in Table 1. Despite the porosity of Si₃N₄, the flexural strength measured was 418 MPa due to strong neck formation between β-Si₃N₄ grains. The hardness of Si₃N₄ was measured as 10.9 GPa and for ZrO₂ 13.7 GPa. If the hardness of ceramic material is high, the wear of opposing natural teeth can be observed. The lower hardness of Si₃N₄ can provide an advantage over ZrO₂ based dental ceramics.

Color shade of samples

Table 2 shows the measured L*, a* and b* values of both ceramics whose thickness values are 0.5, 1.0 and 1.5 mm. L* means the lightness coordinate of the ceramic, chromaticity coordinates of the sample are determined by a* and b* values. L* ranges from 0 (absolute black) to 100 (absolute white). Positive a* shows red when negative (−a*) means green. Positive b* indicates the yellow and negative b* represents blue. Lower L* values were measured for Si₃N₄ compared to ZrO₂ for all thicknesses. The photos of porous Si₃N₄ and ZrO₂ samples can be seen in Fig 2. In spite of lower L* values of Si₃N₄, it has still whitish color that can be used for dental restorations. Also, dense Si₃N₄ sample was included to the figure for comparison. Dark coloration was obtained as the density of ceramic increased. According to Vita classical shade guide (in Fig. 2), the shades of the Si₃N₄ and ZrO₂ samples were determined as C4 and A1, respectively, for all thicknesses. Even though the shade of Si₃N₄ was in the darker range of the guide, the color is acceptable for the restorative dental applications²⁴,²⁵.

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**Table 2**  
L*, a* and b* values for ZrO₂ and Si₃N₄ at different thicknesses. (Average ± standard deviation)

| Thickness (mm) | 0.50       | 1.00       | 1.50       |
|---------------|------------|------------|------------|
| ZrO₂          |            |            |            |
| L*            | 98.10±2.85 | 97.50±2.50 | 95.90±1.87 |
| a*            | −2.20±1.36 | −2.10±0.95 | −2.90±1.36 |
| b*            | 11.00±3.10 | 11.30±2.51 | 7.71±3.89  |
| Si₃N₄         |            |            |            |
| L*            | 31.70±8.14 | 30.30±12.40| 23.30±6.00 |
| a*            | 2.46±1.98  | 2.51±1.99  | 3.62±1.51  |
| b*            | 11.30±3.77 | 11.10±3.11 | 13.50±2.70 |
Table 3 Fracture pattern distribution (as Number) of samples

| Sample              | Adhesive failure | Cohesive failure | Mixed failure |
|---------------------|------------------|------------------|---------------|
|                     | Dentin-cement    | Ceramic-cement   |               |
| ZrO2                | 4                | 1                | 1             | 4             |
| Si₃N₄               | 1                | 8                | —             | 1             |
| Si₃N₄+silane        | 5                | 1                | 2             | 2             |

Shear-bond strength evaluation
The average SBS for Si₃N₄ with coupling agent, ZrO₂ without coupling agent, and Si₃N₄ without coupling agent were 8.44±2.98 MPa, 7.42±1.92 MPa and 2.24±1.15 MPa, respectively (Fig. 3). One-way ANOVA showed a highly significant difference among the experimental groups (p<0.001). Dunnett multiple comparisons test showed no significant difference between Si₃N₄ with coupling agent and ZrO₂ without coupling agent (p=0.776). Si₃N₄ without coupling agent was significantly lower than the other groups (p<0.001).

Fracture patterns of test groups are given in Table 3. Half of the fracture patterns were adhesive failures as four adhesive failures between dentin and resin-cement, one adhesive failure between ceramic and resin-cement were observed for ZrO₂. Also, there are four mixed and one cohesive failures for this group. Again mostly adhesive failure (9/10) was seen in Si₃N₄. Si₃N₄+silane showed adhesive failure (five within dentin and cement and one within ceramic and cement).

Radiopacity evaluation
Radiographic images of the specimens and the radiointensity values are shown in Fig. 4. The ZrO₂ specimens had the highest radiointensity values. Tukey multiple comparison test showed that there was no significant difference among the ZrO₂ specimens regardless of the sample thickness, meaning at these thicknesses, ZrO₂ is almost completely opaque to X-rays. There was also no significant difference between 0.5 mm Si₃N₄ and A1, 1 mm Si₃N₄ and A1 and 1.5 mm Si₃N₄ and A2.

DISCUSSION
Densification and phase development
The main challenge in using Si₃N₄ as a dental restorative material is its gray-black color. In this study, by introducing porosity into Si₃N₄ ceramics, the color was successfully tailored. The common approach to produce porous ceramic is partial sintering, where restricted sintering condition forms a uniform porous structure. In this study, porous Si₃N₄ was obtained by using lower sintering additives (5 wt%) lower sintering temperature (1,700°C) and shorter sintering duration (1 h). SEM observation of the sample shows that the microstructure was identical to that observed with partially sintered ceramic. Fine pores were observed between the typical rod-like β-Si₃N₄ grains. These pores also indicated that sintering was finished before full consolidation took place. Instead of rounded grains, β-Si₃N₄ grains had flat sides due to lower amount of liquid content during the
sintering stage. Substantial changes observed in grains as the volume fraction of liquid (generally 2–5 vol%) is limited, a flat shape is developed in the contact regions of surrounding grains. The flat tip of grains formed sharp-edged pore shape as seen in Figs. 1a and b. During the partial sintering, particles of powder compact are bonded either via surface diffusion or evaporation–condensation processes. A strong neck formation was observed.

**Mechanical characterization**

Glass ceramics, glass infiltrated ceramics, polycrystalline Al2O3 and ZrO2 have been used in all ceramic dental restorations as core materials. Depending on the type of ceramic, flexural strength ranges from 150 to 1,500 MPa. None of these core materials contain porosity and the flexural strength depends on the intrinsic behavior of each ceramic. Porosity is one of the flaws that results in stress concentration, and hence, reduces the strength in ceramics. Since Si3N4 bars were tested in as-fabricated form (i.e., without polishing), higher standard deviation was observed in the flexural strength measurements. Despite its porous nature, Si3N4 had moderate flexural strength compare to their dense counterparts. The strong neck formation between β-Si3N4 grains, the intertwined distribution of these grains and crack deflection potential of rod-like β-Si3N4 are the reasons for observed moderate strength of porous Si3N4. This rod-like grains provide in-situ toughening mechanism to Si3N4 ceramic. Deflection of the crack along the boundaries of these specific grains, bridging of a propagating crack or pulling-out are the mechanisms to reduce the energy of crack and provide higher fracture toughness compare to other ceramics.

The strength of the ZrO2 samples was also lower than the values reported in the literature. The test was conducted according to standard used for advanced ceramics. The mechanical characterization of dental materials is done according to the ISO 6872 standards, where smaller specimens are used. The probability of finding a bigger flaw or more number of defects in a larger ceramic body is higher compared to smaller size. This size difference can be the reason of observed lower strength of ZrO2.

Hardness is another critical mechanical property in restorative materials. The lower hardness of Si3N4 compared to ZrO2 is an important benefit for restorative applications. As the hardness difference between the enamel and the restorative material becomes higher, wear related problems can be experienced in the opposing natural tooth.

**Color shade of samples**

The optical properties are an important aspect of dental restorative materials. The color shade of the materials depends on many variables, such as, crystal morphology, grain size, grain boundary, porosity, etc. For industrial applications of Si3N4, the material is usually produced in a dense form. (Testing of silicon nitride ceramic bearings for total hip arthroplasty) The shade of the dense Si3N4 is relatively dark, gray, sometimes close to black. This limits the use of dense Si3N4 as a restorative material. However, due to the porous nature of the Si3N4 produced in this study, suitable shade (C4) for restorative use was obtained.

**Shear-bond strength evaluation**

A significant difference in SBS was observed between the Si3N4 ceramics luted to dentin with and without a silane coupling agent pre-treatment. The adhesive system used in this study, Panavia Cement SA, is an MDP monomer containing adhesive. This monomer has an M-R-X structure, where M is a metacryl group, R is the carbon chain and X is an acidic phosphate group. Acidic phosphate reacts with the metal oxides, such as ZrO2, Al2O3. Since Si3N4 is thermodynamically unstable under oxidative conditions, its surface is always covered with a 3 to 5 nm thick oxide layer. Due to this oxide layer, Panavia Cement SA could not form a chemical bond with the Si3N4. For silica based ceramics, a silane coupling agent can be used between the ceramic and adhesive material. As silane molecules are activated, methoxy (-OCH3) groups are replaced by hydroxyl (-OH) groups and they directly react with the hydroxyl groups that exist on the surface and covalent bonds are formed via a condensation reaction. This explains the effect of silane coupling agent on the SBS of Si3N4.

**Radiopacity evaluation**

Dentin and Al have equal radiopacity and the radiopacity of enamel is nearly twice than the radiopacity of Al with the same thickness values. This study showed that radiointensity of Si3N4 was only slightly higher than Al, indicating that the radiopacity of Si3N4 is comparable to that of dentin. Lower radiointensity means partial radiolucent behavior. This provides a significant advantage for a dental material in post-operative process. The low radiopacity of Si3N4 will enable for both the restoration and the surrounding tissues to be imaged using plain radiography.

**CONCLUSION**

Up to now, it has been accepted that the dark-gray color of dense Si3N4 ceramics limits their application in restorative dentistry. This study investigated the potential use of porous Si3N4 for all ceramic dental restorations as a core material and results were compared with a commercial ZrO2 ceramic. Some critical parameters were characterized to show the benefits of Si3N4 as a dental restorative ceramic. The color of Si3N4 was tailored by the porosity introduced and a color shade suitable for restorative applications was obtained. The flexural strength of Si3N4 was measured as 418 MPa despite the open porosity content of nearly 10.54%. The hardness of Si3N4 was 10.9 MPa whereas ZrO2 had 13.7 MPa, which reduces the risk for wearing of natural teeth compared to ZrO2. Shear bond strength test indicated that the usage of coupling agent for Si3N4 is essential. When coupling agent was used, Si3N4 had similar shear bond strength to ZrO2. The radiolucent
behavior of Si₃N₄ shown here will enable for both the restorations and the surrounding tissues to be imaged using plain radiography. The results of this study show that with tailored manufacturing methods, Si₃N₄ can be considered as a dental restorative material.

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