

Effect of sintering holding time on the properties and low-temperature degradation behaviour of manganese oxide-doped Y-TZP ceramic

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The sintering of yttria-tetragonal zirconia polycrystals (Y-TZP) is commonly carried at a predefined temperature using a long holding time of 2 hours. This often has resulted in grain coarsening which affects the mechanical properties of the sintered body and low temperature degradation (LTD) behaviour of the ceramic when exposed to moist environment. In this research, the effect of using a short holding time of 1 min. during sintering coupled with small amounts (0.5 and 1 wt%) of manganese oxide, MnO₂ as dopant on the mechanical properties and LTD behaviour of 3 mol% Y-TZP were investigated. The results showed that the mechanical properties improved significantly with the addition of 0.5 wt% MnO₂ for the 1-min. and 12-min. holding time samples when compared to 2 hours holding time sintered at the same temperature of 1350 °C. Nevertheless, regardless of the holding time employed, the 1 wt% MnO₂ addition was not effective in improving the mechanical properties and ageing resistance of Y-TZP ceramic.

Key words: Y-TZP, Sintering, Zirconia, Dopant addition, Degradation.

Introduction

Zirconia ceramics have been reported as one of the most important ceramic materials and have been used in a wide range of applications. They exhibit the phenomenon of allotropy and exist in three polymorphic modifications at different temperatures shown below.



In 1975, Garvie *et al.* [1] highlighted the possibilities of transformation toughening mechanism in certain zirconia ceramics, which make them highly sought-after for industrial applications. However, phase transformation takes place causing noticeable volume changes. The addition of stabilizer such as MgO, CaO and CaO to zirconia (ZrO₂) allows the generation of multiphase materials whose microstructure at room temperature generally consists of cubic zirconia with tetragonal precipitates, subsequently known as partially stabilized zirconia or PSZ [2, 3]. On the other hand, the addition of yttria (Y₂O₃) in amounts between 2.5 to 3 mol% in the zirconia resulted in the retention of a fully tetragonal structure at room temperature [4, 5]. This

ceramic is known as yttria-stabilized tetragonal zirconia polycrystals or Y-TZP [6].

Y-TZP possesses excellent strength, enhanced fracture toughness as well as good wear resistance [7, 8]. The aesthetics and biocompatibility nature of Y-TZP over metallic materials have led to its widespread use in orthopaedics and dental equipment [9, 10]. The excellent mechanical properties of Y-TZP can be accounted for by its ability to undergo a stress-induced phase transformation from metastable tetragonal phase to monoclinic symmetry at room temperature. This transformation is generally accompanied by 3-5% volume expansion which causes compressive stresses around the tip of an advancing crack, thus making it difficult for further crack propagation. This mechanism which is operative in Y-TZP is known as the transformation toughening phenomenon [11, 12].

One of the major drawback of Y-TZP ceramic is the detrimental impact of *t-m* phase transformation when the ceramic is exposed in humid environment, a phenomenon subsequently known as low temperature degradation (LTD) or ageing [13,14]. This typically occurs between temperatures of 100 °C to 400 °C [15, 16]. The LTD was first observed by Kobayashi *et al.* [17] who claimed that exposure of Y-TZP in humid atmosphere exhibited slow *t-m* phase transformation that started at the free surface of the material. This was followed by micro- as well as macro-cracking and eventually massive structural deterioration to the material. Many studies have been devoted towards suppressing the

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devastating effect of LTD and the deterioration in mechanical properties of Y-TZP [18, 19].

One method that has been performed consistently to suppress LTD is the use of sintering additives such as Al_2O_3 [20, 21], CuO [22, 23], MnO_2 [24], Nb_2O_5 [25] and Fe_2O_3 [26]. It has been established in the literatures that monoclinic nucleation starts at grain boundary regions and propagates towards the bulk of the material. Thus, the sintering additives adopted aim at modifying the grain boundary region [27, 28]. In addition, sintering additives have also been proven to improve the mechanical properties of Y-TZP ceramics and is the most effective way to promote densification at relatively low temperature. For instance, Zhao *et al.* [29] used CeO_2 and GeO_2 as additives in Y-TZP and found that the ageing effect in the doped samples was reduced significantly compared to the undoped sample after ageing at 200 °C for 72 hours. Ramesh and Gill [30] also revealed that the addition of 0.05 wt% CuO on 2.5 mol% Y-TZP yielded only ~40% monoclinic phase after 200 hours of hydrothermal ageing at 180 °C compared to ~80% monoclinic content in the undoped samples. In addition, the bulk density and fracture toughness of the CuO -doped Y-TZP drastically improved compared to those of the undoped sample. Besides CuO , other transition metal oxides such as manganese oxide (MnO_2) has also been employed as sintering additives in Y-TZP to aid low-temperature sintering and to suppress LTD [28, 31].

Sintering of Y-TZPs has often been carried out at high temperature for a holding time of 2 hours or more [28, 32]. Although high sintering temperature produced relatively good densification, their implementation with long holding time resulted in extreme grain coarsening and low mechanical properties. For example, Kim *et al.* [25] compared the difference between sintering holding times of 1 hour (at 1500 °C) and 5 hours (at 1550 °C) on the ageing behaviour of the sintered 3 mol% Y-TZP samples. After ageing in air for 100 hours, sample held for 5 hours obtained ~80% monoclinic phase while only 10% was achieved for sample held for 1 hour. This was mainly attributed to the large increment of grain size from 0.50 μm to 0.77 μm as holding time increased. Ramesh *et al.* [12] compared the differences between short sintering holding time of 12-min. and the conventional 120-min. or 2 hours holding time on the densification and mechanical properties of undoped and 1 wt% MnO_2 -doped 3 mol% Y-TZP. They found that the shorter sintering holding time was beneficial in aiding densification without causing deterioration in mechanical properties and tetragonal phase stability.

Therefore, in this present work, the effects of MnO_2 doping and short sintering holding times of 1-min. versus 12-min. on the densification, mechanical properties and ageing behaviour of 3 mol% Y-TZP ceramics are reported. The results are compared with the undoped

samples and the conventionally used 120-min. or 2 hours holding time at sintering temperature of 1350 °C.

Experimental Procedure

Sample Preparation

The 3 mol% Y-TZP powder supplied by Kyoritsu Corporation, Japan was used as starting material designated hereafter as undoped. In this work, high purity manganese (IV) oxide (MnO_2) (R&M Chemicals, UK) content of 0.5 wt% and 1 wt% was mixed with the as-received 3Y-TZP powder by planetary ball milling. Milling was performed at a speed of 450 rpm for 40 minutes, using 5 mm zirconia balls. Ethanol was used as mixing medium. After the milling process, the slurry obtained was dried in an oven at 60 °C overnight. The dried powders were then ground and sieved through a 212 μm mesh sieve.

Discs samples ($\phi 20 \times 3$ mm) and rectangular bar samples ($4 \times 13 \times 32$ mm) were compacted using uniaxial pressing at 3 MPa followed by cold isostatic pressing at 200 MPa (Riken Seiki, Japan). In the present work, the sintering temperature was kept constant at 1350 °C because of the excellent properties obtained for this ceramic in previous studies [28]. The sintering was performed in air atmosphere at heating and cooling rates of 10 °C/min using a standard rapid heating tube furnace (LT Furnace, Malaysia). Different sintering holding times of 1 min., 12 min. and 120 min. were evaluated. Prior to characterization, the sintered samples were ground on one face using graded series of SiC papers (120, 240, 600, 800 and 1200) followed by polishing with 3 μm and 1 μm diamond paste to produce an optical reflective surface.

Characterization

The undoped and MnO_2 -doped 3Y-TZP powders as well as the sintered compacts were characterized by X-ray diffraction (XRD: PANalytical Empyrean, Netherlands) using $\text{Cu-K}\alpha$ radiation to determine the presence of tetragonal (*t*) and monoclinic (*m*) contents. XRD patterns were scanned from 2θ of 25 ° to 43 ° in steps of 0.02 °. The (*m*) phase content was determined using the method developed by Toraya *et al.* [33].

The bulk density (ρ) of the sintered samples was measured by water immersion method based on Archimedes principle. The relative density was calculated by taking the theoretical density of Y-TZP as 6.09 g/cm³. The Young's modulus by sonic resonance was determined on rectangular samples using a commercial testing instrument (GrindoSonic: MK5 "Industrial", Belgium) based on ASTM Standard C1259-2008e1 [34].

The hardness (H_v) of the polished sintered 3Y-TZP samples was measured using a Vickers hardness tester (Mitutoyo AVK-C2, USA). A diamond indenter was used with an applied load of 10 kgf and loading time

for 10 seconds. Five measurements were performed on each sample and the average value was taken. Fracture toughness (K_{IC}) of the samples was determined based on the average crack lengths obtained from the Vickers indentations made using the equation derived by Niihara *et al.* [35].

The microstructure of the polished surface sample was observed using a scanning electron microscope (SEM: Hitachi TM3030 Tabletop Microscope, Japan). For the SEM observation, the samples were thermally etched at a temperature 50 °C below its sintering temperature for 30 minutes to expose the grain boundaries. The average grain size of the samples was determined from the SEM images using a line intercept method developed by Mendelson [36]. The hydrothermal ageing was performed in an autoclave containing superheated steam at 180 °C/10 bar for a period up to 200 hours. The extent of the surface transformation to (*m*) phase was determined by XRD analysis.

Results and Discussion

The (*t*) and (*m*) content of the starting Y-TZP powder were not altered with the addition of MnO₂ i.e. the (*m*) phase was about 14% whereas the (*t*) was about 86%. Regardless of dopant addition and different holding times, all the sintered bodies exhibited a fully tetragonal phase after sintering.

The effect of sintering holding time at 1350 °C on the relative densities of both undoped and MnO₂-doped Y-TZPs is shown in Fig. 1. The results showed a vast improvement in relative density of Y-TZP with the addition of 0.5 wt% and 1 wt% of MnO₂ at short sintering holding time of 1-min. Both the MnO₂-doped Y-TZP achieved approximately 97% of relative density in contrast to the 94% for the undoped ceramic. The benefit of MnO₂-doping in terms of densification has been reported in the literatures [24, 28, 31]. It is perceived that the presences of solid solution of MnO₂ increased the lattice defects in the zirconia crystal structure. As a result, diffusion activation energy is

reduced. Moreover, substitution of Mn²⁺ cations onto the Zr sites resulted in fast diffusion paths within the single grains, and therefore improving densification [31].

However, at a holding time of 12-min. and 120-min., the relative density of undoped samples is higher than that of MnO₂-doped Y-TZP samples. For sintering holding time of 12 min., all three different samples showed comparative relative density, in the range of 97-98%. On the other hand, at 120 min. holding time, relative density of the undoped sample increased up to 99%, whilst a slight improvement was observed in the relative densities of both the MnO₂-doped samples when compared to that obtained for 12 min. holding time. It should be noted that the relative density of the 1 wt% MnO₂-doped sample was generally lower than that of 0.5 wt% MnO₂-doped Y-TZP at all holding times. This could be attributed to the development of cubic phase in the tetragonal matrix as reported previously by Ramesh *et al.* [28].

The effect of sintering holding time and MnO₂ addition on the Young's modulus (*E*) of Y-TZP is shown in Fig. 2. In general, Young's modulus trend for the undoped samples correlated well with the relative density shown in Fig. 1, in which the *E* values increased as sintering holding time increased from 1-min. to 120 min. On the other hand, the MnO₂-doped samples showed completely different Young's modulus trend compared to their relative density. The undoped samples attained higher *E* value of ~188 GPa compared to that of others for sintering holding time of 12 min. and 120 min. This is mostly attributed to their high relative densities as depicted in Fig. 1. Interestingly, the highest *E* value of ~190 GPa was achieved for the 0.5 wt% MnO₂-doped Y-TZP when sintered using the short holding time of 1-min.

On the other hand, high amount of MnO₂ (i.e. 1 wt%) was detrimental to the Young's modulus, regardless of sintering holding time as they consistently performed worse than those of undoped and 0.5 wt% MnO₂-doped samples. This observation is in agreement with that reported in the literatures when high amounts of MnO₂

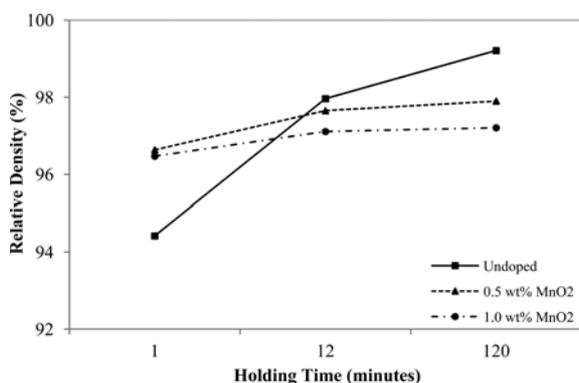


Fig. 1. Relative density (%) variations of 3Y-TZP samples at different MnO₂ content sintered at 1350 °C for different holding times.

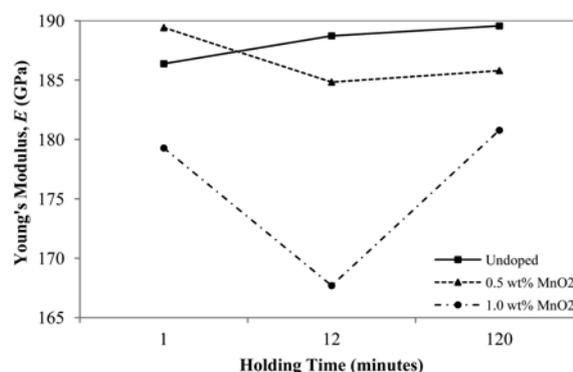


Fig. 2. Variation of Young's Modulus, *E* (GPa) of undoped and MnO₂-doped 3Y-TZPs sintered at 1350 °C for different holding times.

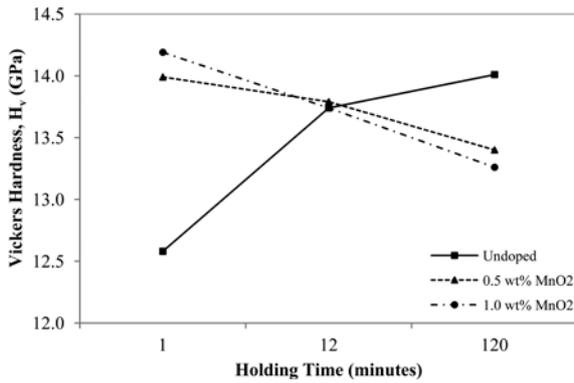


Fig. 3. Relationship between Vickers hardness, H_v (GPa) of 3Y-TZP samples and sintering holding time, sintered at 1350 °C.

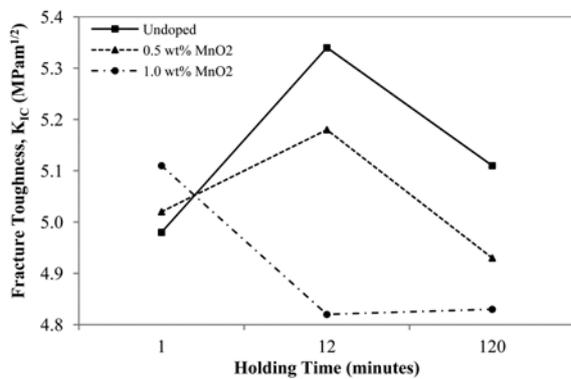


Fig. 4. Fracture toughness, K_{IC} (MPam^{1/2}) variations of undoped and MnO₂-doped 3Y-TZPs sintered at 1350 °C for different holding times.

(1 wt% or more) is incorporated in the Y-TZP matrix [28, 37].

The effects of sintering holding time and MnO₂ additions on the Vickers hardness and fracture toughness of Y-TZP are shown in Fig. 3 and Fig. 4, respectively.

The Vickers hardness trend for the undoped Y-TZP in Fig. 3 is in good agreement with the relative density trend shown in Fig. 1. This increase in hardness from 12.6 GPa to 14 GPa as the holding time increased from 1 min. to 120 min. is attributed to the increasing relative density obtained, particularly the 99% relative density reported for the 120 min. holding time. The beneficial effect of adding MnO₂ in Y-TZP can be observed for the short sintering holding time of 1-min. as shown in Fig. 3. A very high hardness of 14 GPa and 14.2 GPa were measured for the 0.5 wt% and 1 wt% MnO₂-doped samples, respectively. As the sintering holding time increased to 12 min., the hardness values of both MnO₂-doped samples were comparable to that of undoped sample. On the other hand, as sintering holding time increased further to 120 min., the hardness of both the MnO₂-doped samples decreased to ~13.2 GPa whilst the undoped sample exhibited a high value of ~14 GPa.

The fracture toughness variation with sintering holding time is shown in Fig. 4. The highest fracture toughness was achieved at ~5.35 MPam^{1/2} for the undoped sample

Table 1. Effect of sintering holding time and MnO₂ addition on the average tetragonal grain size (μ m) of 3Y-TZPs.

MnO ₂ content (wt%)	Grain Size (μ m)		
	1-min	12-mins	120-mins
0 (Undoped)	0.33	0.33	0.40
0.5	0.35	0.32	0.41
1.0	0.35	0.33	0.43

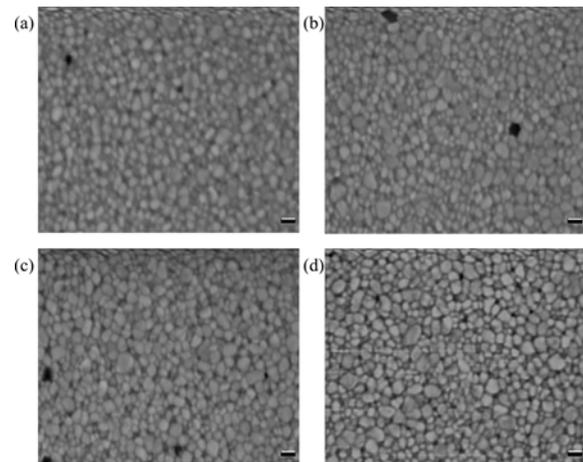


Fig. 5. SEM microstructures of samples held for 12-mins of (a) Undoped (b) 0.5 wt% MnO₂-doped (c) 1.0 wt% MnO₂-doped and (d) Undoped sample held for 120-mins (bar = 0.3 μ m).

when sintered using the 12 min. holding time. At holding time of 1 min and 120 min., fracture toughness reduced to approximately 5-5.1 MPam^{1/2}. Similar trend is observed for the 0.5 wt% MnO₂-doped Y-TZP which recorded a fracture toughness of about 5 MPam^{1/2} at 1 min. holding time followed by an increase to ~5.2 MPam^{1/2} at 12 min. holding time before declining to ~4.9 MPam^{1/2} at 120 min. holding time. On the other hand, addition of 1 wt% MnO₂ exhibited the highest fracture toughness of about 5.1 MPam^{1/2} when sintered using the short sintering holding time of 1-min. Further increased in holding time however was not beneficial as the fracture toughness declined to below 4.85 MPam^{1/2}.

The grain size has often been reported as one of the major influence in the low-temperature degradation (LTD) behaviour of Y-TZP ceramic. In this study, the grain size as measured from the SEM micrographs of polished samples are presented in Table I. In addition, typical microstructures of Y-TZPs sintered using the 12 min. holding time and 120 min. holding time for the undoped sample are shown in Fig. 5.

It can be observed from Table 1 and Fig. 5 that the addition of MnO₂ had negligible effect on grain size of Y-TZP ceramic i.e. the grain size varied between 0.32-0.35 μ m for sintering holding times of 1 min. and 12 min., and between 0.40-0.43 μ m for sintering holding time of 120 min. However, the grain sizes of the undoped and MnO₂-doped Y-TZPs were observed to increase by about 22-25% to when sintered using the 120 min.

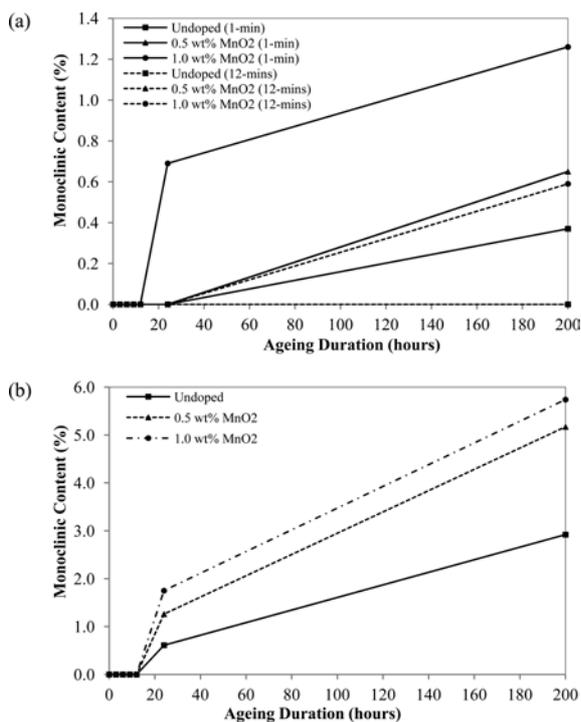


Fig. 6. Effect of MnO₂ addition on amount of monoclinic (*m*) content upon ageing for 3Y-TZP samples at (a) 1-min and 12-mins and (b) 120-mins sintering holding time.

holding time. This shows that the short holding time is effective in terms of controlling the tetragonal grain size of the sintered Y-TZP.

The development of (*m*) phase resulting from LTD after exposure in superheated steam at 180 °C for up to 200 hours is shown in Fig. 6. Both the 1 min. holding time and 12 min. holding time samples exhibited better resistance to ageing (Fig. 6(a)), developing less than 1.3% monoclinic content after 200 hours of exposure in superheated steam. In comparison, the Y-TZP sintered using the 120-min. holding time exhibited higher monoclinic content (2 to 6%) after 200 hours of exposure as depicted in Fig. 6(b). The improved ageing resistance observed for the 1 min. and 12 min. holding time samples could be attributed to the smaller grain sizes of the sintered body as shown in Table 1.

The addition of MnO₂ into 3Y-TZP can be either beneficial or detrimental to their ageing behaviour [38]. This was supported by the ageing behaviour of different MnO₂ contents shown in Fig. 6. The 0.5 wt% MnO₂-doped samples performed better than 1 wt% MnO₂-doped samples for all three different holding times. This was in agreement with previous studies which used sintering additives such as MnO₂ [28,37], CuO [30, 39] and Nb₂O₅ [25]. Ramesh *et al.* [39] reported that higher amount of CuO (i.e. 0.20 wt% compared to 0.05 wt%) was not effective in suppressing the ageing-induced phase transformation. The authors suggested that the reduction of yttria enrichment at the

grain boundaries due to yttria dissolution into the CuO-rich phase resulted in the instability of the Y-TZP during exposure in superheated steam.

In the present work, for the 1 min. holding time, undoped and 0.5 wt% MnO₂-doped sample attained relatively low monoclinic content (<1%) while the 1 wt% MnO₂-doped ceramic exhibited higher phase transformation. Although both the 0.5 and 1 wt% MnO₂-doped samples had almost similar grain size of 0.35 μm, the higher (*m*) content attained by the 1 wt% MnO₂-doped sample could possibly be associated with increasing amount of yttria dissolution into the MnO₂-rich phase during sintering. As a result, the amount of yttria present at grain boundary regions would be insufficient to prevent the tetragonal grains from hydroxyl attack during ageing.

Conclusions

In this present work, the effects of addition of MnO₂ as sintering additive and short holding time of 1 min. and 12 min. compared to the conventionally applied 120 min. have been investigated on the mechanical properties and ageing resistance of 3 mol% Y-TZP. It was revealed that for the undoped samples, although short sintering holding time of 1-min. and 12 min. was not beneficial in terms of densification and mechanical properties as compared to 120 min. hold sample, the samples achieved relative good ageing resistance, especially for 12 min. hold sample mainly due to the lower grain size.

Densification and mechanical properties drastically improved upon addition of small amount of MnO₂ (i.e. 0.5 wt%) at short sintering holding time of 1 min. and 12 min. It was found that the 0.5 wt% MnO₂-doped sample attained relative density of above 97%, Young's modulus of ~185 GPa, Vickers hardness of > 13.5 GPa and fracture toughness of ~ 5.2 MPam^{1/2}. Besides, these Y-TZPs exhibited excellent ageing resistance as no monoclinic content was observed after 200 hours of exposure in superheated steam. This is attributed to their low grain size of 0.32 μm. On the other hand, addition of 1 wt% MnO₂ was found to be less effective regardless of holding time in terms of enhancing the densification as well as improving the ageing resistance of Y-TZP. This study has shown that an overall improved densification, mechanical properties and ageing resistance were obtained for the 0.5 wt% MnO₂-doped Y-TZP when sintered using a 1 min. and 12 min. holding times.

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