Low-calcination temperatures of magnesia partially stabilized zirconia (Mg-PSZ) nanoparticles derived from local zirconium silicates

Kristanto Wahyudi1,4, Eneng Maryani1,4, Ferry Arijadi1, Atiek Rostika2, Dedek Yusuf6, Ria Julyana Manullang1, Suyanti3 and Rifki Septawendar1,4,∗

1 Center for Ceramics, Ministry of Industry of Indonesia, Jl. Akhmad Yani 392, Bandung 40272, Jawa Barat, Indonesia
2 Department of Chemistry, University of Padjadjaran, Jl Raya Bandung Sumedang Km 21 Jatinagor Sumedang 45361, Jawa Barat, Indonesia
3 Center for Science and Accelerator Technology, National Nuclear Energy Agency of Indonesia, Jl. Babarsari 6101, Yogyakarta, Indonesia
4 The authors contributed equally as the main contributor of this paper. All authors read and approved the final paper.

∗ Author to whom any correspondence should be addressed.
E-mail: rifkiseptawendar@gmail.com and rifki@kemenperin.go.id

Keywords: Mg-PSZ, local zircon, nanoparticles, a facile templating method, low calcination temperatures

Abstract
Partially stabilized zirconia (PSZ) exhibits excellent physical, mechanical, electrical, chemical, thermal, and bioactive properties. Therefore, it is frequently used as a material for thermal barrier coatings, refractories, oxygen-permeating membranes, dental and bone implants. In this study, magnesia-partially stabilized zirconia nanoparticles were successfully prepared from zirconium silicates and MgSO4 assisted with PEG-6000 via a facile templating method. The MgO concentration was varied from 1%–10% in wt% of ZrO2. Zirconium silicates were initially converted to Zr-precursor solution, exhibiting pH 3. Then, the appropriate amount of the Mg-precursor was mixed with the proper amount of the Zr-precursor solution. A 10%(w/v) PEG-6000 solution was added into the PSZ precursor solution at a ratio of the precursor-to-PEG volumes of about 15:1 under stirring and heating, resulting in a very fine white gel. The gel was filtered, dried, and then calcined at elevated temperatures of 600, 800, and 1000 °C. The characteristics of the final product were then evaluated. According to the experimental results, the MgO concentration influences the ZrO2 phase transformation at elevated calcination temperatures. In this study, the lower the MgO dopant concentration added into ZrO2, the more stable the t- ZrO2 phase in PSZ samples at high temperatures. However, the MgO presence is detected as periclase in all samples with a very low peak intensity at elevated calcination temperatures. The obtained PSZ samples consist of nanoparticles and high agglomeration, some of particles exhibit elongated and rod-like shapes. The PEG existence during the PSZ preparation has restrained particle interaction and aggregation of the as-synthesized PSZ samples, leading to PSZ nanoparticles evolution.

1. Introduction
Partially stabilized zirconia (PSZ) is known as an interesting material due to its fascinating physical, mechanical, electrical, chemical, thermal, and bioactive properties [1–7], such as good flexural strength [8, 9], high toughness [6, 7, 9, 10], excellent wear resistance [4, 8, 11, 12], high thermal shock resistance [9, 13], good ionic conductivity [14, 15], inert, and biocompatible [16–18]. Thus, PSZ frequently finds applications in thermal barrier coatings [19–22], refractories [23–25], oxygen-permeating membranes [14], dental and bone implants [17, 18, 26, 27], etc.

Particularly, PSZ comprises of two or more different phases of ZrO2. It can be mixtures of the t-, the c-, and the m-ZrO2. The stabilized ZrO2 is usually obtained with the addition of the common dopants such as yttria
Materials used in this study were the local zircon of West Borneo, Na₂CO₃, and magnesia (MgO). Yttria-partially stabilized zirconia (Y-PSZ) exhibits more superior properties than magnesia-partially stabilized zirconia (Mg-PSZ). However, it is relatively quite expensive. As comparison to YSZ, previous studies showed that Mg-PSZ revealed promising characteristics in some aspects, namely better mechanical and thermal properties [14], good stability in low-temperature degradation (LTD) of ZrO₂ ceramics [9], and a comparable thermal-expansion coefficient [20]. Hence, Mg-PSZ offers a promising and low-cost sophisticated material for advanced applications.

Many methods have been proposed in the synthesis of Mg-PSZ, including a conventional solid-state reaction [1, 28], precipitation and co-precipitation techniques [5, 29, 30], a polymeric precursor route [31], sol-gel processing [26, 32–34], Pechini method [33, 35], sugar technique [36], plasma spray synthesis [33, 37], electrospinning [38], and microwave heating technique [39]. Nevertheless, most of these methods use high purity grade chemicals such as salt and alkoxide precursors and may require specific design instruments, resulting in high cost and less economic values. For instance, the usage of a local raw material like zircon sand as ZrO₂ precursor, is suggested and should reduce the cost in the preparation of Mg-PSZ. Besides, to the best of our knowledge, there was only one paper that reported the preparation of Mg-PSZ from zirconium silicates. Thus, in other words, the studies on the synthesis of Mg-PSZ using zirconium silicate as the Zr-precursor are still hardly ever reported.

Quadling et al. used zircon sand to prepare fused Mg-PSZ by a carbothermal reduction method then followed by melting process with pure magnesia [40]. However, they reported that the final product consisted of some secondary phases in the Mg-PSZ aggregates because of the impurity’s interaction of the reduced zircon sand with MgO [40]. In the present paper, we report the preparation of Mg-PSZ nanoparticles from local zircon assisted with PEG-6000 as a polymer template through a facile templating method.

Our previous study successfully synthesized Mg-PSZ nanoparticles from salt precursors via sugar technique [36]. The organic compound was used as a masking template to reduce the tendency toward agglomeration of the as-synthesized particles, leading to the formation of nano-sized Mg-PSZ [36, 41]. Another organic compound that can be used as a masking template or a dispersant is an organic polymer, such as polyethylene glycol, for instance. Apart from being a dispersing agent, polyethylene glycol can also be employed as a one-dimensional structure directing template [42–44]. PEG comprises of the oxylene groups (−CH₂ − CH₂ − O−) in its chain structure which is terminated by the hydroxyl groups at the edges. These functional groups facilitate PEG to interact with the other molecules consisting of the hydroxyl groups through the hydrogen bonding. The interaction between PEG and the other molecules such as metal hydroxides would retard the reaction of among metal hydroxide molecules, resulting in the dispersed particles and slower particle growth. This phenomenon is expected leading to the nanoparticle evolution. At high temperatures, the PEG decomposes and turns into volatile matters, leaving zirconia particles in the nanostructures. Thus, the objective of this study is to prepare Mg-PSZ nanoparticles from local zircon (ZrSiO₄) assisted with PEG-6000 as a masking polymer via a facile templating method. At first, the local zircon was converted into zirconia precursor. The chemical compositions of both of the materials were analyzed using an XRF method. The zirconia precursor was then used in the synthesis of Mg-PSZ nanoparticles with various doping concentrations. In this study, the calcination temperature applied is defined at lower temperatures of 600 °C, 800 °C, and 1000 °C. Hence, the present study also aims to evaluate the influence of the dopant concentration on the phase transformation of ZrO₂ of the resulting PSZ at low calcination temperatures. The characteristics of the as-synthesized and the final products were assessed including the infra-red spectrum, mineral phases, and microstructures.

2. Methods

2.1. Materials and instruments

Materials used in this study were the local zircon of West Borneo, Na₂CO₃, (NH₄)₂CO₃, a 96% H₂SO₄ solution, a 10% NH₄OH solution, carboxyl methyl cellulose (CMC), PEG-6000, and MgSO₄ · 7H₂O from Merck. Inc. All materials were used without further purification. The laboratory apparatus used in this study was an IKA dual speed mixer model RW 20 DZM with the maximum speed of 2000 rpm, a gas furnace with the maximum temperature of 1300 °C, and a Nabertherm electric furnace with the maximum temperature of 1700 °C. Meanwhile, the instruments that used for the material characterization were a Thermo ARL 9900 X-ray fluorescence instrument, a Bruker D8 Advance x-ray diffractometer, a Prestige 21 Shimadzu FT-IR Spectrophotometer, a JEOL-JSM-IT300LV SEM, and a JEM-1400 120 kV TEM.

2.2. Synthesis of Mg-PSZ nanoparticles from ZrSiO₄ assisted by PEG through a facile precursor-templating method

The synthesis of Mg-PSZ nanoparticles from ZrSiO₄ was initially carried out by destruction of ZrSiO₄ with Na₂CO₃ via a modified sodium carbonate sintering method [45, 46]. All preparation steps of the method were...
fully adopted in this work, except the hydrolysis of zirconium salt. Nevertheless, hydrolysis of the obtained zirconium salt was conducted at pH 5, resulting in a very fine white gel. Then, the gel was dried in an oven at 100 °C. The dried gel was washed with cool and hot water in order to remove the water-soluble impurity of Na₂SO₄ [44]. Then, the final product was calcined at 1000 °C and characterized by the XRF method to evaluate its chemical composition. In addition, the ZrO₂ content in the local zircon-based zirconium hydroxide precursor was approximately about 15%.

The original pH of the prepared zirconium hydroxide gel precursor was pH 5. Before the synthesis of Mg-PSZ using PEG template was carried out, the gel precursor pH was initially adjusted to pH 3. A 96% H₂SO₄ solution was used to dissolve the gel precursor, resulting in a zirconium salt solution at pH 1. Hereafter, a proper amount of (NH₄)₂CO₃ was added into the precursor salt solution until its pH attaining pH 3. Magnesium salt solution was prepared separately from the gel precursors. Amounts of the MgO dopant were varied from 1 to 10 wt% of ZrO₂, namely 1wt% 5PSZ, 5wt% 10PSZ, and 10wt% 10PSZ. The amount of MgSO₄ · 7H₂O weighed had to produce the desire weights% of MgO. According to the design composition, the appropriate amount of the Mg-precursor solution was then added into the Zr-precursor solution under vigorous stirring, resulting in a homogenous solution. Then, a 10% (w/v) PEG-6000 solution was added into the PSZ precursor solution at a ratio of the precursor-to-PEG volumes ((Vₚ/V_pEG)) of about 15:1. The solution mixture was stirred under heating at 100 °C for 3 h, resulting in two phases which consisted of very fine white gel and a clear solution. The precursor gel was filtered and dried in an oven at 100 °C. The dried gel was washed with cool and hot water, and dried in an oven at 100 °C. The as-synthesized PSZ was characterized using the FT-IR spectroscopy and then was calcined at elevated temperatures of 600, 800, and 1000 °C. The final product was evaluated including mineral phases and microstructures.

2.3. Characterization of the as-synthesized and the calcined PSZ samples
In this study, the chemical composition of local ZrSiO₄ and the prepared ZrO₂ precursor gel were determined using a Thermo ARL 9900 x-ray fluorescence system. A Prestige 21 Shimadzu FT-IR Spectrophotometer was used to collect typical FT-IR spectra of PEG-6000, the as-synthesized 10PSZ, and the calcined 10PSZ. Meanwhile, particular phases of ZrO₂ in each sample at elevated calcination temperatures were investigated using a Bruker D8 Advance x-ray diffractometer at 40 kV, 40 mA with a Cu/Kα (λ = 1.54060 Å) radiation source. The diffraction patterns were scanned from 10.00 to 90.00 (2θ) with a step size of 0.020. The typical microstructures of all calcined PSZs were observed using a JEOL-JSM-IT300LV SEM and a JEM-1400 120 kV TEM.

3. Results and discussion
3.1. Synthesis of PSZ nanoparticles from zircon assisted with PEG-6000
Zirconium hydroxide precursor was synthesized from local zircon of West Borneo using our method in the previous work, it was a modified sodium carbonate sintering method [45, 46]. All preparation steps of the method was fully adopted in this work, except the hydrolysis of zirconium salt. In this work, it was carried out at pH 5, resulting very fine white gels of zirconium hydroxides in the solution. However, it comprises of two types hydroxides, such as ZrO(OH)₂ and ZrO(OH)₂ · xH₂O [44]. The phenomena that occur during the preparation of the zirconium hydroxide precursor can be briefly explained as follows [45, 46].

\[
\text{ZrSiO}_4 + 2 \text{Na}_2\text{CO}_3 \xrightarrow{\text{at } T 1000 ^\circ C} \text{sodium zirconates} \cdot \text{sodium silicates} + 2\text{CO}_2\text{g} \quad [46, 47]
\]

\[
\text{sodium zirconates} \cdot \text{sodium silicates} \xrightarrow{xH_2O} \text{sodium zirconates} + \text{sodium silicates} \quad [46, 47]
\]

\[
\text{Na}_2\text{ZrO}_3 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{ZrOSO}_4 + \text{Na}_2\text{SO}_4 + 2 \text{H}_2\text{O} \quad [46, 47]
\]

At pH 5, ZrOSO₄ was hydrolyzed, leading to the formation of a mixture of

\[
\text{(ZrO(OH)₂ + ZrO(OH)₂ · xH₂O) fine white gelatinous precipitates} \quad [45]
\]

In the preparation of PSZs, the mixture of gel precursors in reaction (4) was then converted to ZrOSO₄ (pH 1) with the addition of H₂SO₄ (reaction (5)). Then, the pH of the salt precursor was adjusted to 3 with the addition of (NH₄)₂CO₃, resulting in ZrO(OH)₂ (reaction (6)).

\[
\text{ZrOSO}_4 + 2\text{H}_2\text{O} \xrightarrow{(\text{NH}_4)_2\text{CO}_3 + \text{pH } 3} \text{ZrO(OH)₂ + (NH}_4)_2\text{SO}_4 + \text{CO}_2\text{g} + \text{H}_2\text{O} \quad [46, 47]
\]
ether groups of the organic compound [44]. In addition, since the synthesis of PSZ was conducted at pH 3, the polyether of PEG-6000 was hydrolyzed in the existence of sulfuric acid and water, resulting in the degradation of the polymer [44]. The Mg-precursor used in this work was the water-soluble of MgSO₄, thus producing Mg²⁺ ions in the precursor solution. When the PSZ precursor solution was mixed with PEG-6000 under stirring and heating for 3 h, the Zr-precursor reacted with the degraded template to form white gelatinous precipitates of zirconium ethylene glycolates. In a case, Mg²⁺ ions were expected to penetrate the gel. Therefore, this phenomenon should describe the formation of the as-synthesized Mg-PSZ compound. However, the PEG existence during the Mg-PSZ synthesis reduces the inclination for agglomeration in the as-synthesized Mg-PSZ particles. During calcination at elevated temperatures, the organic template was decomposed and burnt out as volatile compounds, leaving the residue of Mg-PSZ particles. At the high temperatures over 500 °C, magnesium oxide (MgO) reacted with the metathetically formed ZrO₂ to produce a solid solution and stabilized the ZrO₂ in the form of either on the cubic or the tetragonal phases [36, 47].

Table 1. The FT-IR spectra elucidation on pure PEG-6000, the as-synthesized 10PSZ, and the calcined 1PSZ and 10PSZ.

| Vibration modes     | Wavenumber (1/cm) |
|---------------------|-------------------|
| νC–O PEG-6000       | 1002.9            |
| νC–C PEG-6000       | 842.0             |
| δCH PEG-6000        | 1644.8, 1360.1, 1344.0 |
| δCH PEG-6000        | 1470.5, 1455.6    |
| νCH₂ PEG-6000       | 2881.0, 963.2     |
| νC–O–C PEG-6000     | 1146.0            |
| νOHER PEG-6000      | 1280.1            |
| The Zr–O bond      | 786.9, 617.7, 439.8 |
| The Mg–O bond       | 617.7             |
| νZr–OH              | 1207.0, 1087.8    |
| νMg–OH              | 1404.2            |
| –O–H,(hydrogenbonding) | 3255.8   |
| The Si–O bond       | 900–1100          |

Figure 1. The results of FT-IR identification of PEG-6000 and the as-synthesized 10PSZ (a); and the calcined 1PSZ and 10PSZ.
Figure 1 demonstrates the FT-IR spectra characteristics of PEG-6000 and the as-synthesized 10PSZ (a); and the calcined 1PSZ and 10PSZ, showing the transmission bands in the range of 4000–400 cm\(^{-1}\). Meanwhile, table 1 presents the elucidation results of the FT-IR spectra on those samples. The bands in the range of 4000–400 cm\(^{-1}\) indicate some typical stretching and bending vibration modes of chemical bonds on the samples, such as vibration modes of the functional groups of PEG-6000 and vibration modes of the Zr–O metal bonding, as shown in figure 1 and table 1 [43–54]. According to the elucidation results of the FT-IR spectra on the as-synthesized 10MSZ, some bands of them may overlap each other. For instance, the IR bands with low twin peaks at 1720.50 and 1635.64 cm\(^{-1}\) could be attributed to the hydroxyl groups (–OH) on the surface of the zirconia precursor and the bending vibrations of the CH-groups [46]. However, the band of Mg–O showed up at a fingerprint area of 617.72 cm\(^{-1}\), attributing to the stretching vibrations of the Mg–O bonding [49]. This Mg–O band seems to be overlapped with the Zr–O band. Based on figure 1, the intermolecular hydrogen bonding between the Zr-precursor and the organic template in the as-synthesized 10PSZ is not detected in the FT-IR spectrum. The band of the bonding usually appears as a peak shoulder that coincident with the peak of the intramolecular hydrogen bonding [50]. Thus, it can be considered that the ZrO\(_2\)-precursor react with the degraded PEG at the pH synthesis 3, resulting in Zr-(ethylene glycolates), and releasing water molecules under heating. The degradation of PEG at pH 3 could be confirmed by very low-intensity and weak peaks of the CH\(_2\)–stretching vibration at 2921.17 and 2870.738 cm\(^{-1}\). Meanwhile, the common structure of PEG shows a high-intensity and strong peak of the CH\(_2\)–stretching vibration at around 2890 cm\(^{-1}\) as shown by FT-IR spectrum of PEG-6000 in figure 1. This result is in good agreement with the reference [51].

### 3.2. Chemical composition of local zircon and the prepared ZrO\(_2\)-precursor gel

Semi quantitative analysis using an XRF method was conducted to determine the purity of local zircon and the ZrO\(_2\) yield prepared from a local zircon-based zirconium hydroxide precursor after water-washing treatment. Table 2 (the second column) presents the chemical composition of local zircon that used as the zirconia source in this work. The zircon consists of 62.89 wt% ZrO\(_2\) and 32.96 wt% SiO\(_2\). Meanwhile, the major impurities are Al\(_2\)O\(_3\) and HFO\(_2\), accounting for 0.942% and 0.856% in weight percent, respectively. In addition, table 2 (the third right column) shows the ZrO\(_2\) purity obtained after calcination the precursor at 1000 °C, containing 91.43 wt% ZrO\(_2\) as the main component. Meanwhile, the impurities are dominated by SiO\(_2\), Al\(_2\)O\(_3\), and HFO\(_2\), accounting for 2.32%, 1.87%, and 1.22% in weight percent, respectively. However, the yield percentage of ZrO\(_2\) in this work is relatively higher than in our previous work [46]. The presence of SiO\(_2\) and Al\(_2\)O\(_3\) impurities in the ZrO\(_2\) yield should be produced during the hydrolysis of the sintered products in reaction (2). According to reaction (1), since ZrSiO\(_4\) reacted with Na\(_2\)CO\(_3\) at a high temperature, it converted into

![Figure 1](image-url)

Table 2. Semiquantitative result of XRF analysis in local zircon and the ZrO\(_2\) yield prepared from local zircon after calcination at 1000 °C.

| Compound | Local ZrSiO\(_4\) Wt/Wt% | Zirconium hydroxides at 1000 °C Wt/Wt% |
|----------|------------------------|----------------------------------------|
| ZrO\(_2\) | 62.89                  | 91.43                                  |
| SiO\(_2\) | 32.96                  | 2.32                                   |
| Al\(_2\)O\(_3\) | 0.942            | 1.87                                   |
| HFO\(_2\) | 0.856                  | 1.22                                   |
| P\(_2\)O\(_5\) | 0.053             | 0.691                                  |
| CaO      | 0.0565                 | 0.627                                  |
| MoO\(_3\) | 0.301                 | 0.517                                  |
| Fe\(_2\)O\(_3\) | 0.0416         | 0.391                                  |
| Y\(_2\)O\(_3\) | 0.124              | 0.197                                  |
| Cr\(_2\)O\(_3\) | 0.130             |                                         |
| TiO\(_2\) | 0.0628                 | 0.111                                  |
| Na\(_2\)O | 0.107                  | 0.056                                  |
| MgO      | 0.0803                 | 0.0543                                 |
| Yb\(_2\)O\(_3\) | 0.0221           | 0.0392                                 |
| U\(_2\)O\(_5\) | 0.0244            | 0.0330                                 |
| K\(_2\)O  | 0.0106                 | 0.0313                                 |
| CI       | 0.0195                 | 0.0297                                 |
| Er\(_2\)O\(_3\) | 0.0128           | 0.0237                                 |
| La\(_2\)O\(_3\) | 0.0189          |                                         |
| ZnO      | 0.0181                 |                                         |
| Sc\(_2\)O\(_3\) | 0.0092            |                                         |
| Am\(_2\)O\(_3\) | 0.0309           |                                         |
| OsO\(_4\) | 0.0140                 |                                         |
sodium zirconates · sodium silicates and so did the zircon impurities. For instance, the Al₂O₃ contaminant also reacted with Na₂CO₃ at a high temperature, resulting in sodium aluminates. Both sodium silicates and sodium aluminates are water-soluble compounds. They are readily hydrolyzed in water, producing fine gelatinous precipitates of hydroxide compounds, such as Si(OH)₄ and Al(OH)₃. However, although filtration and water-washing treatments were conducted to separate sodium zirconates from the fine hydroxide contaminants, some of them might attach the surface or infiltrate to the inside of the sintered product. Thus, a few of Si(OH)₄ and Al(OH)₃ fine particles join with sodium zirconates in the acid leaching process (reaction (3)), resulting in acid-soluble compounds. Subsequently, they were solidified along with zirconium salts during hydrolysis process at pH 5, producing gelatinous precipitates. The hydroxides of Si and Al turn into the oxides after calcination of zirconium hydroxides at 1000 °C. Therefore, a small amount of them was recorded during the XRF measurement.

3.3. XRD investigation on the mineral phase transformation of PSZ at elevated temperatures

Typical phases of ZrO₂ in PSZ samples with three different concentrations of MgO as the dopant were investigated at elevated temperatures from 600 °C to 1000 °C using a Bruker XRD system. Figure 3(a) demonstrates the XRD identification results on all PSZ samples at ZrO₂ precursor pH 3 and after calcination at 600 °C. Based on figure 3(a), both 1PSZ and 5PSZ samples show similar diffraction patterns of the resulted ZrO₂, revealing the existence of the t- and the c- ZrO₂ phases as according to JCPDS PDF2 No. 791770 and 270997, respectively. Most of the main peaks of both of the t- and the c- phases are overlap. The appearance of the t-ZrO₂ phase is noticed by its diffraction peaks at diffraction angles, 2θ, of 30.40°, 50.25°, 50.74°, and 60.20°, conforming the (101), (112), (200), (211) crystal planes of the t-ZrO₂ structure, respectively. Meanwhile, the c-ZrO₂ phase is expressed by its diffraction peaks at diffraction angles, 2θ, of 30.40°, 50.57°, and 60.34°, affirming the (111), (220), (311) crystal planes of the c-ZrO₂ structure, respectively. Nevertheless, the diffraction pattern of 10PSZ sample clearly differs from the others. At 600 °C, the sample consists of only the single c-ZrO₂ phase, based on JCPDS PDF2 No. 772156 and 800964. It is obviously shown by its peaks at diffraction angles, 2θ, of 30.46°, 50.75°, and 60.43°, corresponding to the (111), (220), (311) crystal planes of the c-ZrO₂ structure. However, all PSZ samples show the existence of periclase, magnesium oxide. Its appearance is noticed by a very low peak at a diffraction angle, 2θ, of 43.07°. It is associated with the reflection of the (200) crystal plane of the c-MgO structure. In this study, based on the XRD results in figure 3(a), some of magnesium oxide (MgO) particles reacted with the metathetically formed ZrO₂ to produce a solid solution and stabilized the ZrO₂ in the form of either on the cubic or the tetragonal phases [36, 47] and some of them that not reacted with ZrO₂ alter into periclase phase at a high temperature of 600 °C.

Figure 3(b) presents the XRD analysis results of all PSZ samples calcined at 800 °C. According to the XRD patterns of all PSZ samples in figure 3(b), there is no significant change in the mineral phase transformation of both 1PSZ and 5PSZ samples, excluding 10PSZ sample. One small peak is identified at a diffraction angle, 2θ, of 59.57° in the XRD pattern of 10PSZ. It is assigned to the reflection of the (103) crystal plane of the t-ZrO₂ structure. The phenomenon indicates phase transformation from the c- to the t-phases of ZrO₂ in 10PSZ sample during heating at 800 °C and then cooling to the ambient temperature. Our findings evidently differ from the report of Duwez et al [55]. They identified the m-ZrO₂ and MgO as the formed phases in the zirconia-magnesia system after firing at temperatures from 600 °C to 900 °C, when using ZrO₂ and MgO as raw materials and the MgO concentrations of about 1–24 wt% [55]. The issue on the different results should be specifically governed by synthesis conditions, such as the type of precursors, template, pH, medium, temperature, and the reaction process. In addition, the XRD analysis results show the existence of MgO phase as periclase still detected in all PSZ samples at 800 °C in this study.

Figure 3(c) shows the XRD characterization results of all PSZ samples after firing at 1000 °C and then cooling to the ambient temperature. All PSZ samples consist of the t- and the m-ZrO₂ in agreement with JCPDS PDF2 No. 791770 and 830944, respectively. The presence of the m- phase in all PSZ samples is indicated by its diffraction main peaks at diffraction angels, 2θ, of 28.41° and 31.48° that associates with the (–111) and (111) crystal planes of the m-ZrO₂ structure, respectively. However, a considerably difference among PSZ samples is noticeably illustrated by 10PSZ sample, showing the m-phase as the major and the dominant phase. The t- and the c- phases of ZrO₂ in 10PSZ sample almost fully transform to the m-ZrO₂ at 1000 °C, but no MgO polymorphs are identified in the sample. Similar phenomenon is also observed in 5PSZ sample. At 1000 °C, the MgO periclase phase in 5PSZ and 10PSZ samples is assumed starting to merge and to react with ZrO₂, generating in a solid solution at higher temperatures than 1000 °C. By contrast, the t-phase relatively remains stable in 1PSZ sample and the MgO periclase phase is still detected at a very low peak intensity. In completion, based on the experimental results, this study finds that the lower the MgO dopant concentration added into ZrO₂, the more stable the existing t- ZrO₂ phase in PSZ sample at high temperatures. Nevertheless, further investigation
especially on the ZrO₂ phase transformation at the sintering temperature of PSZ samples should be helpful to justify all the phenomena during MgO stabilization of ZrO₂ with the present various dopant concentrations.

In addition, according to the XRF measurement results in table 2, the Zr-precursor that used in the synthesis of PSZ nanoparticles in this study consists of major impurities such as SiO₂ and Al₂O₃, accounting for 2.32% and 1.87%, respectively. However, the impurities do not seem to affect the zirconia phase transformation that occurs during the calcination process of the as-synthesized PSZ samples, as according to the XRD results in figure 2. It is probably due to very low content of the impurities, thus they were not identified during the XRD measurements.

Figure 2. The XRD analysis results of all PSZ samples calcined at 600 °C (a), 800 °C (b), and 1000 °C (c).
However, Vasanthavel reported that the existence of SiO$_2$ in the ZrO$_2$-SiO$_2$ binary system assisted the stabilization of the tetragonal phase of ZrO$_2$ through the formation of Si-O-Zr bonds between ZrO$_2$ and SiO$_2$ \[56\].

Table 3 presents the average crystallite sizes of any phases formed in PSZ nanoparticles at every calcination temperature using the Scherrer method, assisted with an XRD software. According to Table 3, the average crystallite sizes of any phases formed in all PSZ samples are below 50 nm.

![Typical SEM images of all PSZ samples calcined at 600 °C.](image)

**Figure 3.** Typical SEM images of all PSZ samples calcined at 600 °C.

**Table 3.** Quantitative results of the average crystallite sizes of any phases formed in PSZ nanoparticles using the Scherrer method.

| Sample | 600 °C | 800 °C | 1000 °C |
|--------|--------|--------|---------|
|        | c-     | t-     | m-      | c-     | t-     | m-      | c-     | t-     | m-      |
| 1PSZ   | 9      | 9      | 13      |        |        |         | 40     | 20     |         |
| 5PSZ   | 9      | 9      | 13      |        |        |         | 28     | 21     |         |
| 10PSZ  | 9      | 13     | 12      |        |        |         | 12     | 26     |         |
Based on figure 2 and the table 3, the tetragonal phase of ZrO$_2$ is stable in PSZ samples after calcination at 600$^\circ$C and 800$^\circ$C. Since PSZ samples at those temperatures consist of nanocrystallite (less than 100 nm), the tetragonal phase can be stabilized at room temperature. It is also named as nanoparticle size effect [47, 57]. Nanocrystalline powders exhibits very huge specific surface area, thus lowering the surface energy. In addition to the characteristic of nanocrystalline powders, more than 50% of the total atoms are on the surface. Subsequently, a larger number of metal-oxygen bonds are going to frail that lead to desorption of lattice oxygen ions, generating much more oxygen ion vacancies. This phenomenon helps to stabilize the tetragonal phase of ZrO$_2$ [57, 58].

3.4. Microstructures of Mg-PSZ

Typical microstructures of all PSZ samples at elevated calcination temperatures were observed by a scanning electron microscope. Figure 3 display the results of SEM analysis in the microstructures of PSZ samples at 600$^\circ$C. The microstructures of PSZ samples at the temperature show that they comprise of ultrafine particles and high agglomeration. Based on figure 3, the as-synthesized PSZ samples exhibit ultrafine particles below 50 nm in sizes after calcination at 600$^\circ$C. Since nanoparticles exhibit large surface areas, they usually attract each other forming agglomerate to reduce the interfacial energy of the system. The proposed attraction forces are van der Waals forces that are essentially stronger in the nanoscale [41]. In addition, as according to figure 3, SEM images of all PSZ samples show miscellaneous microstructures. In addition to spherical particles, rod-like particles and elongated agglomerates can be observed in all PSZ samples in figure 3. Those morphologies are noticed by red marks and yellow arrows in SEM images (figure 3). The existence of the rod-like shape and elongated agglomerate particles should be due to interaction between zirconia precursor and polyethylene glycol during synthesis. In a

![Figure 4. Typical SEM images of all PSZ samples calcined at 800$^\circ$C.](image-url)
case, the polymer serves as a one-dimensional directing template [44]. This phenomenon is obviously observed in the 10PSZ sample, more rod-like shape and elongated agglomerate particles can be found.

Figure 4 presents the microstructures of all PSZ samples at 800 °C, showing ultrafine particles below 50 nm in sizes in general and high agglomeration, as well as all PSZ samples calcined at 600°C. Some of rod-like shape and elongated agglomerate particles also can be found in the microstructures of PSZ samples calcined at 800 °C, which are indicated by red marks. The higher the calcination temperatures applied, the larger PSZ particles produced, as shown in figure 5. Along with the increase of the calcination temperature, the PSZ particles are growing larger, this phenomenon is evidently demonstrated by 10PSZ sample in figure 5. According to the XRD results in figure 2, the tetragonal phase of ZrO₂ in 10PSZ sample almost completely transforms to the monoclinic phase of ZrO₂ at 1000 °C. However, this transformation is followed by 3 to 5% volume increase [59], resulting in larger dimension. Thus, 10PSZ sample consisting of the m-ZrO₂ as the dominant or major phase will exhibit larger particles than the other samples consisting of the t-ZrO₂ as the major phase. This phenomenon is obviously shown by SEM images of 10PSZ sample in figure 5, uniform larger particles of the considered m-ZrO₂ can be found in the morphology of 10PSZ sample at 1000 °C. Meanwhile, the morphology of 1PSZ sample consisting of the t-ZrO₂ as the major phase demonstrates the finest particles of all PSZ samples, as given by SEM images in figure 5.

Figure 6 displays the results of TEM characterization in all PSZ samples after calcination at 800 °C, featuring nanoparticles and agglomeration in the microstructures of all PSZ samples. In addition, some marked areas in the TEM images of PSZ samples unveil elongated and rod-like shapes of PSZ nanoparticles, as shown in figure 5.

Figure 5. Typical SEM images of all PSZ samples calcined at 1000 °C.
In a case, the presence of PEG template during the synthesis of Mg-PSZ diminishes the inclination of the as-synthesized Mg-PSZ particles to agglomerate. PEG 6000 is built up by a lot of ethylene glycol monomers, consisting of ethoxy or oxyethylene structures in its chains and hydroxyl groups at the beginning and at the end of the chain structures. PEG 6000 cleaves at acidic medium and in the presence of a strong acid and water.
generating lower molecular weight PEG, or small units of glycols [44]. However, all types of those degraded PEG contact and attract the molecules of ZrO(OH)\(_2\) through the hydrogen bonding. As a result, the degraded PEG molecules cover the surface hydroxyl groups of the ZrO\(_2\) precursor, resulting in reduced particle interaction and aggregation of the as-synthesized PSZ samples. This phenomenon retards the PSZ particle growth during heating at high temperatures, leading to PSZ nanoparticles evolution. The retarding mechanism of the interaction among ZrO(OH)\(_2\) molecules by the degraded PEG during synthesis of PSZ is concisely proposed in figure 7. The Zr-precursor reacted with the degraded template to form very fine white gels of zirconium ethylene/polyene glycolates. Nevertheless, Mg\(_2^+\) ions were expected to penetrate the gel, resulting in the as-synthesized PSZ compounds. At high temperatures, the organic content of zirconium ethylene/polyene glycolates was burnt out as gases, leaving PSZ particles in the nanostructures.

The TEM observation results in figure 6 confirm the SEM analysis results shown in figure 5, indicating elongated and short rod-like shapes of some nanoparticles in all PSZ samples. The particular microstructures should be generated during the synthesis of PSZ at pH 3. At this point, the PEG degraded at pH 3 behaved as a template as well as a dispersing agent. The degraded PEG reacts with ZrO(OH)\(_2\) molecules through the hydrogen bonding between both the hydroxyl groups of the Zr precursor and the degraded PEG. Under heating, the reaction between PEG and the Zr precursor results in zirconium ethylene glycolates and water molecules. In this situation, the structure directing process of ZrO\(_2\) by the degraded PEG occurs, reconciling the template structure [44].

4. Conclusions

The present study reports the preparation of Mg-PSZ nanoparticles from zirconium silicates and MgSO\(_4\) precursors and assisted with PEG-6000 via a facile templating method. Based on the experimental results in this study, the MgO concentration influence the ZrO\(_2\) phase transformation at elevated calcination temperatures. The lower the MgO dopant concentration added into ZrO\(_2\), the more stable the t-ZrO\(_2\) phase in PSZ sample at high temperatures. However, the MgO presence is detected as periclase in all samples with a very low peak intensity at elevated calcination temperatures. The obtained PSZ samples consist of nanoparticles and high agglomeration, some particles exhibit elongated and rod-like shapes. The existence of PEG during the PSZ preparation has restrained particle interaction and aggregation of the as-synthesized PSZ samples, leading to PSZ nanoparticles evolution.

Acknowledgments

This work was also supported by the 2020 Development of Industrial Technology and Policy DIPA from Center for Ceramics, the Ministry of Industry, the Republic of Indonesia.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Rifki Septawendar https://orcid.org/0000-0003-3754-9120

References

[1] Li J, Peng J, Guo S and Zhang L 2013 Application of response surface methodology (RSM) for optimization of sintering process for the preparation of magnesia partially stabilized zirconia (Mg-PSZ) using natural baddeleyite as starting material Ceram. Int. 39 197–202
[2] Khodaii J, Barzanideh F, Rezaei S M, Adibi H and Sarhan A A D 2018 High-temperature stability of YSZ and MSZ ceramic materials in CaF\(_2\)–MgF\(_2\)–MgO molten salt system J. Am. Ceram. Soc. 101 2074–83
[3] Kong X H, Tang J, Sun R and Liu Q 2012 MgO-PSZ Solid state electrolyte tubes for metallurgical oxygen sensors made by powder injection moulding Adv. Mater. Res. 366 249–52
[4] Deirmina F and Pellizzari M 2020 Mechanical properties and tempering resistance of an ultrafine grained Tool Steel-PSZ composite fabricated by high energy mechanical milling and spark plasma sintering Mater. Sci. Eng. A 786 139428
[5] Garvie R C, Urbani C, Kennedy D R and Mcneuer J C 1984 Biocompatibility of magnesia–partially stabilized zirconia (Mg-PSZ) ceramics J. Mater. Sci. 19 3224–8
[8] Leach CA 1989 A Raman microprobe study of a magnesia partially stabilized zirconia fracture surface J. Mater. Sci. 24 1380–2
[9] Soylemez B, Sener E, Yurdakul A and Yurdakul H 2020 Fracture toughness enhancement of yttria-stabilized tetragonal zirconia polycrystalline ceramics through magnesia-partially stabilized zirconia addition J. Sci. Adv. Mater. Dev. 3 527–34
[10] Jang J H and Lee J 2000 Microstructure and mechanical properties of fine-grained magnesia-partially stabilized zirconia containing titanium carbide particles J. Am. Ceram. Soc. 83 1813–5
[11] Akkus A and Boyraz T 2018 Investigation of wear properties of CaO, MgO added stabilized zirconia ceramics produced by different pressing methods J. Ceram. Proc. Res. 19 249–52
[12] Wischedtal R, Sato K, Brandt G, Schmid T, Sasaki S and Wooldt M 2019 Wear behaviour of MgO stabilized zirconia in hot steam environment up to 400 °C Wear 426–427 428–32
[13] Jiang L, Guo S, Qiao M, Zhang M and Ding W 2017 Study on the structure and mechanical properties of magnesia partially stabilized zirconia during cyclic heating and cooling Mater. Lett. 194 26–9
[14] Yoon S, Van Tyne C J and Lee H 2014 Effect of alumina addition on the microstructure and grain boundary resistance of magnesia partially stabilized zirconia Curr. Appl Phys. 14 922–7
[15] Terracciano A C, De Oliveira S T, Vasu S S and Orlovskaya N 2018 LaCoO3 catalytically enhanced MgO partially stabilized ZrO2 in heterogeneous methane combustion Exp. Thermal Fluid Sci. 90 330–5
[16] Hao L, Lawrence J, Chian K S, Low D K Y, Lim G C and Zheng H Y 2004 The formation of a hydroxyl bond and the effects thereof on bone-like apatite formation on a magnesia partially stabilized zirconia (MgO-PSZ) bioinorganic following CO2 laser irradiation J. Mater. Sci. Mater. Med. 15 967–75
[17] Rahaman M N, Li Y, Bal B S and Huang W 2008 Functionally graded bioactive glass coating on magnesia partially stabilized zirconia (Mg-GPSZ) for enhanced biocompatibility J. Mater. Sci. Mater. Med. 19 2325–33
[18] Hadjiicharalambous C, Mygdale E, Prymak O, Buyakov A, Kulkoiv S and Chatzinikolaidou M 2015 Proliferation and osteogenic response of MC3T3-E1 pre-osteoblastic cells on porous zirconia ceramics stabilized with magnesia or yttria J. Biomed. Mater. Res. Part A 103A 3612–24
[19] Baig M N, Khalid F A, Khan F N and Rehman K 2014 Properties and residual stress distribution of plasma sprayed magnesia stabilized zirconia thermal barrier coatings Ceram. Int. 40 4853–68
[20] Doleker K M, Ogoruluk Y, Ozkan D, Mesekiran N and Kamaroglanli A C 2018 Comparison of microstructures and oxidation behaviors of yttria and magnesia stabilized zirconia thermal barrier coatings (TBCs) Mater. Technol. 52 315–22
[21] Haefz M A E, Akila S A, Khedr M A and Khalil A S 2020 Improving wear resistance of plasma-sprayed calcia and magnesia-stabilized zirconia mixed coating: roles of phase stability and microstructure Sci. Rep. 10 21830 1–14
[22] Hajizadeh-Oghaz M, Razavi R S and Kajhelakay M 2015 Optimizing sol–gel synthesis of magnesia-stabilized zirconia (MSZ) nanoparticles using Taguchi robust design for thermal barrier coatings (TBCs) applications J. Sol-Gel Sci. Technol. 73 227–41
[23] Jiang L, Guo S, Liu Y, Bian Y, Chen S, Zhang X, Yang G and Ding W 2016 Influence of sintering temperature on microstructure and properties of magnesia partially stabilized zirconia ceramics Characterization of Minerals, Metals, and Materials 2015 ed J Carpenter et al (Switzerland: Springer International Publishing) pp 345–51
[24] Jiang L, Guo S, Bian Y, Zhang M and Ding W 2016 Mechanical properties of magnesia partially stabilized zirconia refractory Ceram. Int. 42 10593–8
[25] Jiang L, Guo S, Bian Y, Zhang M and Ding W 2016 Interfacial behaviors of magnesia partially stabilized zirconia with nickel-based superalloy Mater. Lett. 181 313–6
[26] Nakonienczy D, Walke W, Majewska I and Paszenda Z 2014 Characterization of magnesia-doped yttria-stabilized zirconia powders for dental technology applications Acta Biomed. Biomech. 16 99–106
[27] Roy M E, Whiteside L A and Sebastian A M 2017 Retrieved magnesia-stabilized zirconia femoral heads, exhibit minimal roughening and abrasive potential J. Arthroplasty 32 3806–14
[28] Deng W and Li Y 2019 High-temperature electrical properties of polycrystalline MgO-doped ZrO2 Mater. Res. Bull. 113 182–9
[29] Yamagata C and Paschoal J O A 2015 Systematic precipitation of magnesium hydroxide using NH4OH to preparing MgO-PSZ precursor powder Mater. Sci. Forum 805 712–7
[30] Prochazka I, Cizek J, Melkioiva O, Konstantinova T E, Danilenko I A and Yashchishyn I A 2012 Positron annihilation study of zirconia nanocomposites: fabrication methods and applications Mater. Today Sustain. 3–4 10 0007 1–15
[31] Mirtaleh A H and Mammoory R S 2020 Enhanced thermoluminescence of magnesia doped zirconia nanoparticles expose to UV/ beta irradiation Nanotechnol. 31 115601
[32] Hajizadeh-Oghaz M, Razavi R S and Kajhelakay M 2015 Optimizing sol–gel synthesis of magnesia-stabilized zirconia (MSZ) nanoparticles using Taguchi robust design for thermal barrier coatings (TBCs) applications J. Sol-Gel Sci. Technol. 73 227–41
[33] Septawendar R, Sunendar B and Sutardi S 2012 Preparation of magnesia stabilized zirconia nanoparticles at low calcination temperature by a colloidal gel method Journal of the Indonesian Ceramic and Glass 21 44–59
[34] Buyakovka S P, Kalatur S E, Buyakov A S and Kulkoiv S S 2016 Structure and properties of ZrO2–MgO powders IOP Conf. Ser.; Mater. Sci. Eng. 123 012040 1–5
[35] Heuer G, Storti E, Graule T and Aneziris C G 2020 Electrospinning of Y2O3 - and MgO-stabilized zirconia nanofibers and characterization of the evolving phase composition and morphology during thermal treatment Ceram. Int. B 46 12001–8
[36] Chen G, Li Q, Ling Y, Zheng H, Chen J, Jiang Q, Li K, Peng W, Omran M and Gao J 2021 Phase stability and microstructure morphology of microwave-sintered magnesia-partially stabilised zirconia Ceram. Int. 47 4076–82
[37] Quarding A, Vandererre P, Parkes M and Lee W E 2014 Second phase-induced degradation of fused mgo partially stabilized zirconia aggregates J. Am. Ceram. Soc. 98 1364–71
[38] Septawendar R, Setiati A and Sutardi S 2011 Low-temperature calcination at 800 °C of alumina–zirconia nanocomposites using sugar as a gelling agent Ceram. Int. 37 3747–54
[39] Maryani E, Subagio, Nuruddin A, Septawendar R and Purwasastra B S 2015 Effects of aging and temperature parameters, polyethylene glycol (PEG)/Al ratios on the structure directing mechanism of γ-alumina nanofiber-based Indonesian natural kaolin by ultrasonic aging process J. Aust. Ceram. Soc. 54 116–22
Septawendar R, Nuruddin A, Maryani E, Sutardi S and Purwasasmita B S 2018 Synthesis of zirconia 1D nanomaterials from local zircon-based Zr(OH)₄ mediated by PEG-6000 Res. J. Chem. Environ. 22 163–71

Septawendar R, Nuruddin A, Sutardi S, Asri L A T W, Maryani E, Setiawan A R and Purwasasmita B S 2019 Synthesis of one-dimensional ZrO₂ nanomaterials from Zr(OH)₄ precursors assisted by glycols through a facile precursor-templating method Mater. Res. Express 6 065037 1–18

Septawendar R, Sutardi S, Karsono U and Sofiyaningish N 2016 A low-cost, facile method on production of nano zirconia and silica from local zircon in a large scale using a sodium carbonate sintering technology J. Aust. Ceram. Soc. 52 92–102

Septawendar R, Nuruddin A, Sutardi S, Maryani E, Asri L A T W and Purwasasmita B S 2018 Low-temperature metastable tetragonal zirconia nanoparticles (NpMTZ) synthesized from local zircon by a modified sodium carbonate sintering method J. Aust. Ceram. Soc. 54 643–54

Septawendar R, Purwasasmita B S and Sutardi S 2013 Effect of the hydrolysis catalyst NH₄OH on the preparation of calcia stabilized zirconia with sugar as a masking agent at low temperatures J. Aust. Ceram. Soc. 49 101–8

Zhang H-C, Kang B-H, Sheng X and Lu X 2019 Novel bio-based pomelo peel/polyethylene glycol composite phase change material for thermal energy storage Polymers 11 2043 1–17

Ansari A, Ali A, Asif M and Shamsuzzaman 2018 Microwave-assisted MgO NP catalyzed one-pot multicomponent synthesis of polysubstituted steroidal pyridines New J. Chem. 42 184–97

Septawendar R, Nuruddin A, Asri L A T W, Abdullah M R, Adhika D R, Maryani E and Purwasasmita B S 2019 Nano cellulose-assisted synthesis of zirconia nanorods from local zircon-based Zr(OH)₄ precursors J. Ceram. Soc. Japan 127 864–8

Lin Z, Han X, Wang T and Li S 2008 Effects of adding nano metal powders on thermooxidative degradation of poly(ethylene glycol) J. Therm. Anal. Cal. 91 709–14

Pilarska A, Wysokowski M, Markiewicz E and Jesionowski T 2013 Synthesis of magnesium hydroxide and its calcinates by a precipitation method with the use of magnesium sulfate and poly(ethylene glycols) Powder Technol. 235 148–57

Zahir M H, Rahman M M, Irshad K and Rahman M M 2019 Shape-stabilized phase change materials for solar energy storage: MgO and Mg(OH)₂ mixed with polyethylene glycol Nanomaterials. 9 1773 1–21

Shameli K, Ahmadi M B, Jazayeri S D, Sedaghat S, Shabanzadeh F, Jahangirian H, Mahdavi M and Abdollah Y 2012 Synthesis and characterization of polyethylene glycol mediated silver nanoparticles by the green method Int. J. Mol. Sci. 13 6639–50

Duwez P, Odell F, Frank H and Brown F H 1952 Stabilization of zirconia with calcia and magnesia J. Am. Ceram. Soc. 35 107–13

Vasanthavel S, Derby B and Kanaan S 2017 Tetragonal to cubic transformation of SiO₂ stabilized ZrO₂ polymorph through dysprosium substitutions Inorg. Chem. 56 1273–81

Shukla S and Seal S 2005 Mechanisms of room temperature metastable tetragonal phase stabilisation in zirconia International Materials Reviews 50 1–20

Santos V, Zeni M, Bergmann C P and Hohemberger J M 2008 Correlation between thermal treatment and tetragonal/monoclinic nanostructured zirconia powder obtained by sol-gel process Rev. Adv. Mater. Sci. 17 62–70

Simba B G, dos Santos C, Strecker K, Alves de Almeida Junior A and Adabo G L 2016 Recovery of tetragonal phase from previously transformed Y-TZP Mater. Res. 19 829–33