

## Study of the Synthesis of Zirconia Powder from Zircon Sand obtained from Zircon Minerals Malaysia by Caustic Fusion Method

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**Abstract:** The zircon powder from Zircon Minerals Malaysia is a pure premium grade zircon sand milled 1.5  $\mu\text{m}$  that contain  $\text{ZrSiO}_4$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{Fe}_2\text{O}_3$ . The monoclinic zirconia powders were synthesized from the zircon sand of Zircon Minerals Malaysia, by caustic fusion method at calcination temperatures between 500 °C to 800 °C. The as-synthesized zirconia was characterized through X-Ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric and differential thermal analysis (TG-DTA), and X-Ray fluorescence (XRF) techniques. The XRD results show two monoclinic phases of microcrystalline zirconia. Zirconia that was calcined at 600 °C obtained the highest value of  $\text{ZrO}_2$ , which was 54.48%; followed by zirconia calcined at 700, 800, and 500 °C, which obtained the  $\text{ZrO}_2$  values of 53.58, 52.41, and 51.53%, respectively, based on the XRF analysis. As-synthesized zirconia showed monoclinic phases where the surface areas were 0.0635g, 0.135, 0.0268, and 0.0288  $\text{m}^2/\text{g}$ , for zirconia calcined at temperatures of 500, 600, 700, and 800 °C, respectively. The surface structure of the powder that had been calcined at 600 °C showed similarities with the commercial zirconia. The similarities of the synthesized zirconia and commercial zirconia showed that the zirconia powder could be synthesized using zircon sand by caustic fusion method, even though the content of zirconia was lower compared to that of the commercial zirconia powder.

**Keywords:** zirconia; zircon sand; monoclinic; caustic fusion method

### ■ INTRODUCTION

Zirconia ( $\text{ZrO}_2$ ) powder is a white crystalline known as zirconium oxide. This powder is chemically inert and can withstand high temperatures, corrosion, and thermal shock [1]. The condition of the zirconia can either be in natural form or processed form. Zirconium oxide is the condition when the zirconia is in the natural form, known as mineral baddeleyite. The zirconia is calcined to high temperatures to produce zirconia oxide. Many researchers are interested in studying the zirconia powder because it is widely used in ceramic materials and many applications, such as in dentistry, scaffold bone tissue engineering, and

enamels [2]. The melting point of the natural zirconia as mineral baddeleyite is high, which is 2715 °C, and its boiling point is 4300 °C, which makes the toughness of the zirconia very high [3]. Zirconia has unique properties because of its complex and temperature-dependent phase transition. Pure zirconia exists in three crystal phases: monoclinic, cubic, and tetragonal, depending on the temperature [4]. The material can have sharp edges and a very smooth surface when the powder is in fine grain size. However, the weakness of the zirconia in its physical characteristics is shown during phase change, when it is heated [5]; the addition of stabilizers can overcome this problem. Yttria partially stabilized zirconia

exists when the yttrium oxide is added as a stabilizer, making it one of the solutions in solving this problem [6].

There are several methods to produce zirconia powder, such as hydrothermal oxidation, thermal decomposition, precipitation, and hydrolysis [7]. The method used to produce different characteristics of zirconia powder is based on the desired product. The best result obtained for zirconia powder is using chemical routes, but it is not an economical method for industrial manufacturing compared to the conventional milling method [8]. However, the high-quality nanometer-sized powder is obtainable using the technology of precipitation. Nevertheless, these powders are relatively expensive even though it produces high purity zirconia. Zircon can be used to overcome the problem because zircon is the main mineral precursor. Zircon is the main type of heavy mineral species, and it can be found at the beach along the coast of Brazil [9]. In industrial minerals, zircon is commercially important. The use of zircon in the production of zirconia is quickly increasing because it is capable of resisting high temperatures and chemical attacks, creating good refractory for furnaces, steel ladles, and foundry sand used [10]. The production of zirconia is simple, and it requires low capital and operational cost by concentrating the zircon through caustic fusion [11-12]. These facts show that the caustic method is essential for compound production. The fusion method is generally used to synthesize the zirconia from zircon. In this method, different chemicals can be used, such as sodium hydroxide, and calcium carbonate. However, sodium hydroxide is commonly used in caustic fusion method for the production of zirconium oxide or zirconia. Thus, in this study, to synthesize the zirconia powder, zircon sand will be used to produce high purity and economical zirconia by using caustic fusion method.

## ■ EXPERIMENTAL SECTION

### Materials

Table 1 shows the chemical composition of Australian Zircon sand obtained from the Zircon Minerals Malaysia. The commercial zirconia powder was obtained from Vistee Technology Services.

**Table 1.** Chemical composition of zircon sand

Name of substances	Composition percent (%)
Zirconia + Hafnia (ZrO <sub>2</sub> + HfO <sub>2</sub> )	64.2
Silica (SiO <sub>2</sub> )	33.8
Alumina (Al <sub>2</sub> O <sub>3</sub> )	0.90
Titania (TiO <sub>2</sub> )	0.14
Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> )	0.06

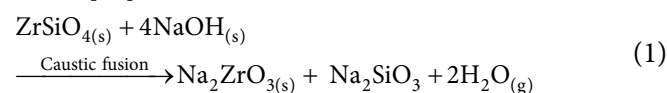
### Instrumentation

Analysis were conducted to evaluate the physical and chemical characterizations of all of the synthesized zirconia powders. The thermal behavior of the powders was analyzed by thermogravimetric and differential thermal analysis (Mettler Toledo TGA/DSC SDTA851). The powders were then heated from room temperature to 1000 °C at a heating rate of 10 °C/min in a flowing nitrogen atmosphere. Ultima IV Rigaku X-Ray diffractometer was used at a scan speed of 2 °C/min over a scan range between 10°–90° to examine the phase that is present in the powder. The particle size distribution of the powder was measured using Malvern Instrument type Mastersizer 2000. Brunauer–Emmett–Teller (BET) analysis was used to measure the specific surface area, and X-Ray fluorescence (XRF) PAN Analytical Axios was used to determine the chemical composition in the powder. The surface structure of the powders was assessed using a scanning electron microscopy (SEM) image (Zeiss LEO 1525).

### Procedure

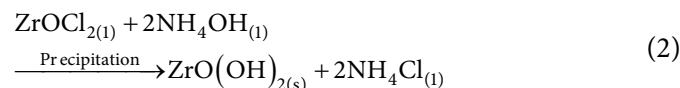
#### Synthesis of zirconia powder

The zirconia was synthesized by using the caustic fusion method. NaOH was weighed at 30 g and zircon at 33 g [13]. The weight was determined by calculating the number of moles according to the chemical reaction below [13]:

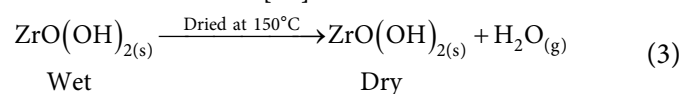


Next, the acid leaching method was used to produce ZrOCl<sub>2</sub> by dissolving the mixture in 120 mL of 5 M HCl solution. The process was conducted at 85 °C for 30 min. Then, the ZrOCl<sub>2</sub> produced was reacted with

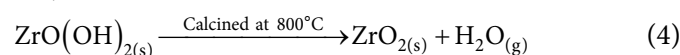
$\text{NH}_4\text{OH}$  1 M until the pH of the solution becomes 9 to obtain the  $\text{Zr}(\text{OH})_4$ .



The process was done by stirring at 90 °C. The  $\text{Zr}(\text{OH})_2$  was produced after 24 h, and then filtered and washed using hot water to get a pH solution of 7. Before the zirconia powder was obtained by the calcination process, the residue was heated at 150 °C for 3 h to remove the moisture content [13].



The calcination process was done at 800 °C for 5 h and repeated with different temperatures which were 500, 600, and 700 °C.



## ■ RESULTS AND DISCUSSION

### Thermal Analysis

Fig. 1 shows the TG-DTA curves of the hydrous zirconia,  $\text{ZrO}(\text{OH})_2$  after it was dried at 150 °C. The TG-DTA curve exhibited several endothermic peaks below 1000 °C which indicates that the samples obtained would

be denatured at a temperature of 765.8 °C. However, the sample structures illustrate that the samples calcined at more than 700 °C had started to melt, as shown in Fig. 7(c), and hardened when they were cooled at room temperature. Based on the DSC curves, the melting point of  $\text{ZrO}(\text{OH})_2$  was 59.94 °C. The melting point of  $\text{ZrO}(\text{OH})_2$  should be 318 °C [13]. This result showed that the presence of impurity components added during the synthesis of  $\text{ZrO}(\text{OH})_2$ , such as ammonium ion, had accelerated the degradation of the polymeric network, while the chloride ions that had affected the thermal stability of caustic fusion were not significant, compared to the ammonium ions.

### Crystallization

Fig. 2 shows XRD patterns of the samples that were prepared at different temperatures in the calcination process, which ranged from 500 to 800 °C for both the synthesized and commercial zirconia powders. The X-Ray diffractogram showed two monoclinic phases of nanocrystalline zirconia 28.1° (111), 31.4° (111) (JCPDS card no.78-1807) and tetragonal 30.2° (101), 50.2° (112) and 60.2° (211) (JCPDS card 79-2769) [14].

In Fig. 2(b) to (e), based on the samples used, the X-Ray pattern on the line of the synchrotron beam showed

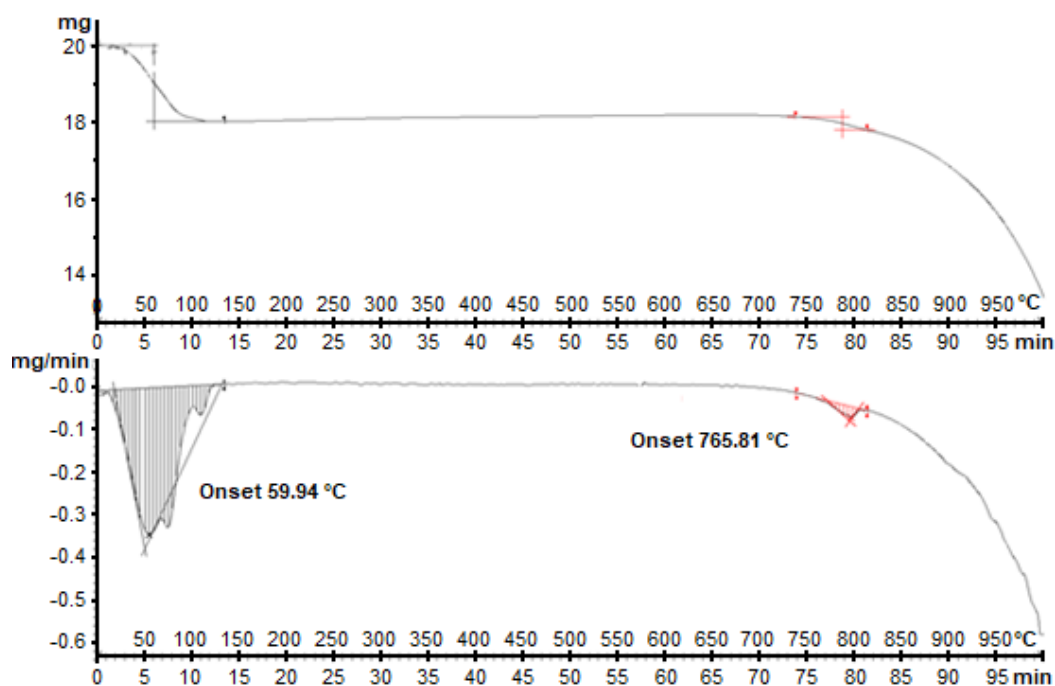
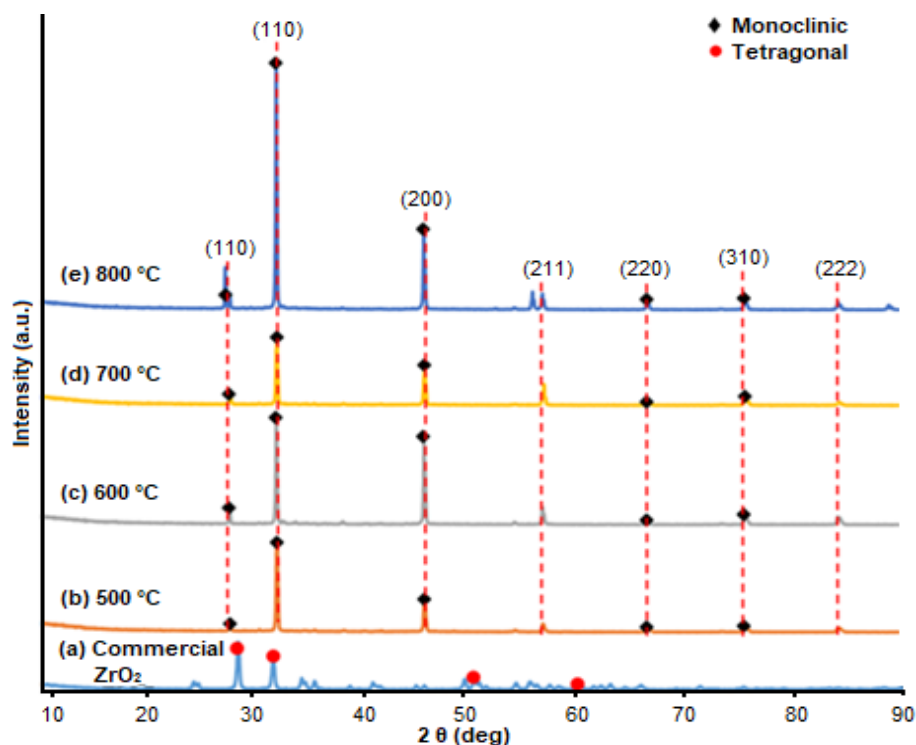


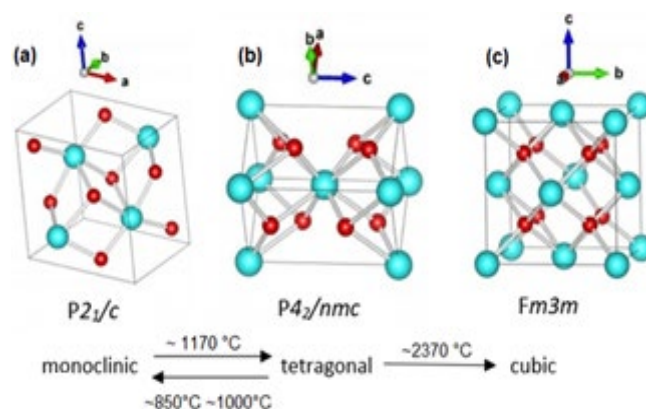
Fig 1. TG-DTA curves of the hydrous zirconia,  $\text{ZrO}(\text{OH})_2$  precipitated after dried at 150 °C



**Fig 2.** XRD patterns for commercial zirconia and hydrous zirconia,  $ZrO(OH)_2$  after calcination at various temperature

that the synthesized zirconia was a nearly pure monoclinic zirconia (> 95%) [15]. The synthesized zirconia did not possess the tetragonal structure because the calcination temperature was not above 1170 °C, based on the XRD pattern obtained. Fig. 3 shows the three crystallographic structures that occurred in pure zirconia [18]. First, the monoclinic form that remained stable until 1170 °C. Second, the tetragonal form that remained stable between 1170 and 2370 °C. Third, the cubic form that remained stable above 2370 °C. The volumetric expansion of 3–5% is related to both martensitic natures in considerable technological importance in the changes of zirconia from tetragonal to monoclinic structure [16]. Afterwards, the significant effect of calcination on the phase purity of the zirconia powder was determined. Thirty two percent of the total zirconia was in the monoclinic phase and above 1170 °C, in which it will totally change to the tetragonal form. Then, during the calcination process, the presence of cations was resulted from the migration of cations when the existing diffusion pathway was inactivated or not fully in the crystalline phase. This is because the transformation process is indicated by the endothermic peak and is irreversible [17].

However, the preparation of synthesized zirconia can affect its structure. The material was prepared using zircon sand and produced at a pH of 10 when the precipitation was formed, which means it was able to obtain a high percentage of monoclinic form. A medium pH range (8–11) could produce monoclinic zirconia, while a low pH (3–5) and high pH range (13–14) produces tetragonal phase based on previous researches [15]. This is because the initial zirconium species are well detached,



**Fig 3.** Zirconia phase transformations. As the temperature increases, the zirconia transforms from (a) monoclinic to (b) tetragonal to (c) cubic [18]

and could probably be because it is a monoatomic species of the zirconium [15]. The application for monoclinic structure can be used for components in refractory materials, molten metal filters, additive to mixed oxide systems, and nozzles and stoppers of transfer/holding ladles.

Meanwhile, the commercial zirconia contained tetragonal zirconia at a high percentage. The commercial zirconia had fully changed from the monoclinic to tetragonal form since the thermal treatment of the commercial zirconia was above 1170 °C. Within the temperature of 1170 to 2300 °C, the zirconia was in a stable tetragonal form [19-20]. The effect of pH can be the main factor for the zirconia produced in the tetragonal phase because it can be obtained at either a low pH (3–5) or high pH (13–14) range [15].

### Particle Size and Morphology

The particle size distribution parameters of the synthesized zirconia powder are shown in Fig. 4. Usually, the most significant aspect in the particle size distribution is the three-point distribution, nominated as  $D_{10}$ ,  $D_{50}$ , and  $D_{90}$  using Eq. (5).

$$S_w = \frac{2.56}{\log_{10} \left( \frac{D_{90}}{D_{10}} \right)} \quad (5)$$

The ideal condition of the value  $S_w$  can either be less than 2 or greater than 7, showing a very broad ( $S_w = 2$  or  $D_{90} = 19D_{10}$ ) or very narrow distribution ( $S_w = 7$  or  $D_{90} = 2.3D_{10}$ ) [21]. Based on the results tabulated in Table 2, the synthesized particle width distributions were 4.52, 2.26, 2.81, and 5.53, where they correspond to a broad distribution because their  $S_w$  was less than 7. For the commercial zirconia, the  $S_w$  value was 2.49. The particle

width distribution and specific surface area of zirconia and commercial zirconia at 600 °C were almost similar, which were 0.1350 and 0.1310 m<sup>2</sup>/g, respectively. The results obtained from this analysis showed that the zirconia powder could be synthesized by using zircon sand. By using commercial zirconia as an indicator, it is possible to determine if the powder produced is similar to the commercial one or otherwise.

Fig. 5 shows that the increase of temperature made the particle size distribution less narrow, except for the synthesis of zirconia at a temperature of 600 °C. Calcination temperature influences the size of the zirconia and densification of the samples. However, in this result, the value of the specific surface area was not consistent. The smaller the size, the larger the specific surface area. The particle size of the powder is directly dependent on the calcination temperature because at high temperatures, shrinkage is likely to occur on the zirconia [22]. From the observation made, the lower the calcination temperature, the narrower the distribution.

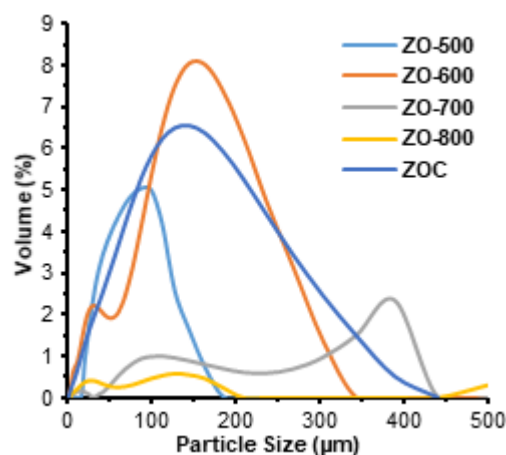


Fig 4. Particle size distribution for synthesized zirconia powder of different temperatures of calcination

Table 2. Parameter of the particle size distribution

ZrO <sub>2</sub> powder	Particle size (µm)			Particle width distribution ( $S_w$ )	Specific surface area (m <sup>2</sup> /g)
	$D_{10}$	$D_{50}$	$D_{90}$		
ZrO <sub>2</sub> 500 °C	38.725	121.380	142.802	4.52	0.0635
ZrO <sub>2</sub> 600 °C	21.928	153.055	299.111	2.26	0.1350
ZrO <sub>2</sub> 700 °C	190.251	930.022	1546.454	2.81	0.0268
ZrO <sub>2</sub> 800 °C	507.257	993.615	1473.014	5.53	0.0288
Commercial ZrO <sub>2</sub>	23.645	110.514	252.177	2.49	0.1310



Primary distribution of the particles are broaden with the equivalent of decreasing volume fraction, as the calcination temperature increases [22]. In Fig. 5, the influence of the particle size on the phase of zirconia is shown when the calcination had been completed to produce zirconia. The calcination temperature had affected the size of the distribution in which the highest surface area was obtained at calcination temperature of 600 °C. This is probably because the zirconia was defined as amorphous zirconia due to its high surface area and the presence of small particles, as well as the presence of the surfactant that can be induced [23]. However, the particle size is probably the influencing factor because the embryonic nuclei is responsible for the nature of the phase obtained. Improvement on the digested zirconia had increased its resistance to thermal calcination of up to 800 °C when compared to the undigested zirconia. As the time of digestion increased, the loss in the surface area decreased with calcination temperature up to 800 °C [24]. Hence, the smallest particle size width was 2.26, which was synthesized zirconia at 600 °C, that also had the largest specific surface area of 0.1350 m<sup>2</sup>/g, in which it is almost similar to that of the commercial zirconia at 0.1310 m<sup>2</sup>/g.

In the BET analysis, the specific surface area,  $S_{BET}$ , and pore distribution were determined. In Table 3, parameters of the BET analysis of the synthesized zirconia are stated.

The highest BET surface area of the synthesized zirconia was 1.8915 m<sup>2</sup>/g, which was calcined at 700 °C, and the lowest surface area was 0.6811 m<sup>2</sup>/g at 600 °C. For the total volume in pores, the highest was 0.00439 m<sup>3</sup>/g, belonging to the synthesized zirconia at 600 °C, and the lowest was 0.00147 m<sup>3</sup>/g. However, as the calcination temperature increased, the total area in pores of the synthesized zirconia also increased.

Fig. 6 shows the surface area against the pore width of the synthesized zirconia calcined at 500, 600, 700, and

800 °C. The pore width widened with increasing calcination temperature, except for the synthesized zirconia calcined at 600 °C. The pore width reached the largest value with an incremental surface area when the synthesized zirconia was calcined at 600 °C. The graph pattern for the synthesized zirconia at 600, 700, and 800 °C were unimodal, and for the synthesized zirconia at 500 °C, it was bimodal. The synthesized powders contained voids or pores. In addition, the particle's slow growth is a direct influence to its loose porous structure

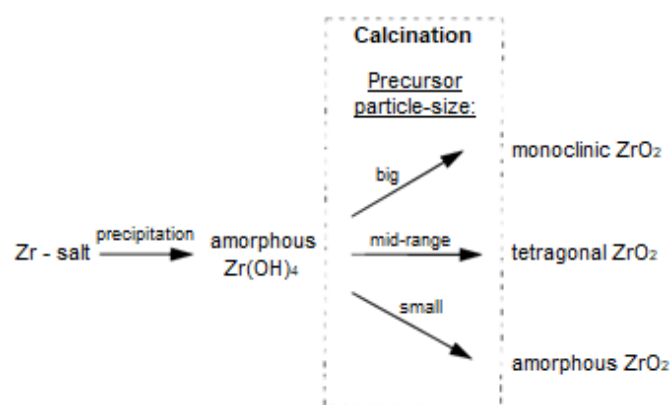


Fig 5. Influence of the precursor particle size on the phase of zirconia [23]

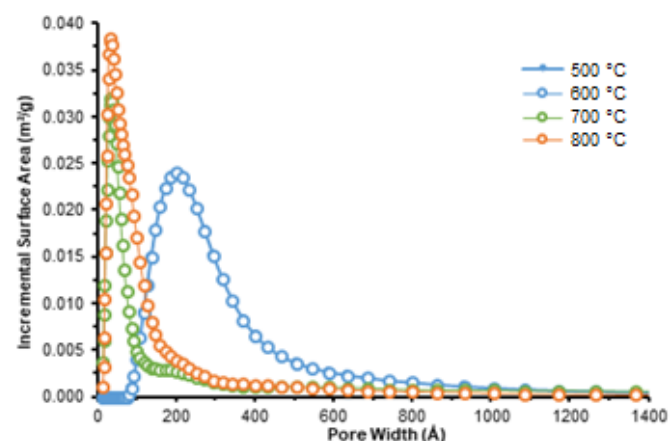


Fig 6. Surface area against pore width of synthesized zirconia at different calcination temperatures

Table 3. Parameter of the BET analysis

ZrO <sub>2</sub> Powder	BET surface area, $S_{BET}$ (m <sup>2</sup> /g)	Total area in pores (m <sup>2</sup> /g)	Total volume in pores (m <sup>3</sup> /g)
ZrO <sub>2</sub> 500 °C	1.0721	0.239	0.00147
ZrO <sub>2</sub> 600 °C	0.6811	0.329	0.00439
ZrO <sub>2</sub> 700 °C	1.8915	0.546	0.00205
ZrO <sub>2</sub> 800 °C	1.5074	0.750	0.00268

and the ability to sustain its amorphous nature during calcination of up to 500 °C [25]. At 600 °C, the intermediate temperature for zirconia transformed the phase from an amorphous to crystalline nature of t-zirconia, and at 800 °C, stabilization was found for t-zirconia with a porous structure [25]. An assumption can be made that ceramics with spherical shape and large pores had caused the presence of particles with hollow spherical shape in the source powder since the average size of the powder corresponds to large pores with an average size in calcined materials [26].

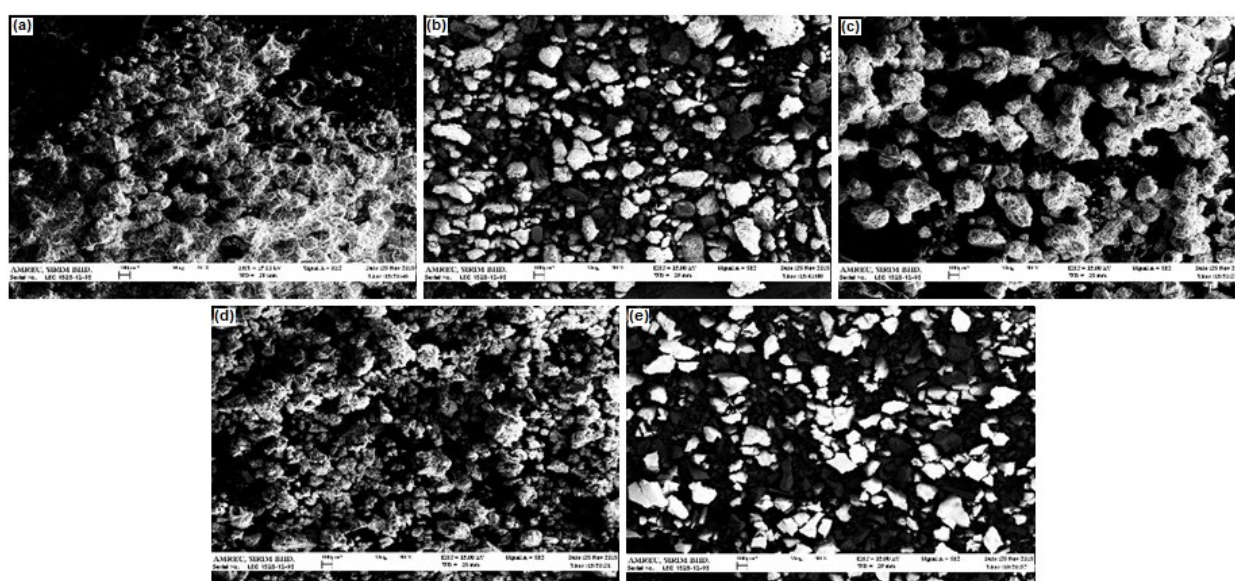
Table 4 indicates the chemical composition of ZrO<sub>2</sub> samples at different calcination temperatures and also the composition of commercial zirconia. The results showed that the synthesized zirconia could produce the highest amount of ZrO<sub>2</sub> at a temperature of 600 °C, which was 54.48%. The amount of Na<sub>2</sub>O in synthesized zirconia was too large. However, the amount of Na substance in zirconia is detrimental to its strength and ionic conductivity, which is an important characteristic of zirconia-based materials [27]. The importance of zirconia containing a high amount of Na can also be seen in when it is used in the thermal barrier, making the high content of sodium in powders acceptable [27]. This can be correlated to the chemical composition of zircon sand in Table 1. The composition of zirconium ions inside the

sand was not pure, due to the presence of other substances which affect the purity of the synthesized zirconia.

Fig. 7 shows the SEM images for the surface and topography of zirconia, synthesized at different calcination temperatures, and also images of commercial zirconia. The structure in Fig. 7(a) showed an amorphous-like structure because it is unlikely to be crystalline. Meanwhile, the differences in Fig. 7(c) and 7(d) are that the shape of the agglomerated powder was reduced when the temperature of calcination increased. Furthermore, Fig. 7(b) showed a similarity in shape with that in Fig. 7(e). The powders calcined at 600 °C had the same shape as commercial zirconia. Based on this observation, the synthesis of zirconia powder can be performed using zircon sand when calcined at 600 °C. However, the structure of zirconia calcined at more than

**Table 4.** Chemical composition of ZrO<sub>2</sub> samples

Samples	XRF Chemical Composition (wt.%)			
	ZrO <sub>2</sub>	Na <sub>2</sub> O	SiO <sub>2</sub>	CaO
ZrO <sub>2</sub> 500 °C	51.53	43.77	7.59	0.18
ZrO <sub>2</sub> 600 °C	54.48	46.40	7.86	0.23
ZrO <sub>2</sub> 700 °C	53.58	41.20	12.09	0.30
ZrO <sub>2</sub> 800 °C	52.41	35.72	16.33	0.36
Commercial ZrO <sub>2</sub>	100	-	-	-



**Fig 7.** SEM images of (a) synthesized zirconia at 500 °C, (b) synthesized zirconia at 600 °C, (c) synthesized zirconia at 700 °C, (d) synthesized zirconia at 800 °C, and (e) commercial zirconia

700 °C showed that the structure becomes denatured because it will start to melt at that temperature.

Based on a previous study, the calcination of local zircon sand from Indonesia using the same method of synthesis, which is the caustic fusion method, at calcination temperature of higher than 500 °C gives good ionic conductivity [13]. The slopes of zirconia calcined between 600 to 700 °C showed the greatest ionic conductivity based on their researches [13]. However, in this study, the synthesis of the zirconia differs from what was performed in the previous study. In the present study, the synthesis of zirconia was conducted using different raw materials, which was the zircon sand supplied from Zircon Minerals Malaysia Sdn. Bhd. However, the same method of synthesis was successfully applied to synthesize the zirconia. The results obtained showed that zirconia calcined at 600 °C had produced an almost similar structure with commercial zirconia. In addition, other characteristics, such as the surface area and pore volume of the synthesized zirconia, were the greatest when compared with other zirconia.

## ■ CONCLUSION

The synthesized zirconia powder can be produced from a caustic fusion method using the raw material of zircon sand. Based on the results using the XRD analysis, BET, SEM, and by investigating the particle size of the synthesized zirconia powder, it was shown that the obtained powder had achieved almost similar characteristics to that of the commercial powder. However, the structure of the synthesized and commercial zirconia based on the XRD analysis was different in which the synthesized zirconia was in a monoclinic structure, while the commercial zirconia was in tetragonal. The SEM images, showed that the structures were the same for both powders. This is proven from observing the particle size width and specific surface area, where results for both powders were almost the same. Hence, the synthesis of zirconia powder using the zircon sand supplied from Zircon Minerals Malaysia Sdn. Bhd. was successful.

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