THE EFFECT OF PH AND CALCINATION TEMPERATURE ON THE ZrO_2 PHASE FORMATION FROM NATURAL ZIRCON SAND OF KERENG PANGI

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ABSTRACT

In this research ZrO_2 has been synthesized from Kereng Pangi zircon sand in Central Kalimantan through alkali fusion-coprecipitation method. Firstly, zircon sand ($ZrSiO_4$) was purified to reduce impurities by magnetic separation, cleaned using an ultrasonic cleaner, soaked/leached with HCl 2 M for 12 hours and leached with HCl at 60 ºC for 3 hours. Secondly, alkali fusion was done with KOH as an alkali. This product was then washed by water and dried before leached with HCl 30% at 90 ºC for 30 minutes to precipitate and seperate Silica from Zircon. ZrO_2 filtrate ($ZrOCl_2$) precipitated with NH_4OH at pH 4, pH 7, and pH 10 forms $Zr(OH)_4$ gel. $Zr(OH)_4$ gel was dried and characterized by DTA-TGA, which was then followed by calcination based on DTA TGA results at temperature ranges of 550 ºC - 700 ºC to produce ZrO_2. XRD results show that single tetragonal phase of ZrO_2 is formed in all variations of pH precipitation and calcination temperature. An analysis using MAUD software show that crystal size reduces as the increase in precipitation of pH. The crystal size results are 110 nm, 66 nm and 48 nm at pH 4, pH 7 dan pH 10 at 700 ºC, respectively. Moreover, XRF results show that ZrO_2 with purity is at around 95.8 % at pH 4 and 96.3 % at pH 7 and pH 10.

Keywords: Alkali Fusion; Coprecipitation; Phase; pH; Crystal Size.

Introduction

Indonesia is very wealthy in natural resources, one of which is mineral. However, the utilization of mineral is still limited to the raw materials, which makes the added value very small compared to the condition where the raw materials are processed into pure or alloy materials, which are ready to enter the industrialization. This potential is then realized by the government which later issued a regulation prohibiting the export of raw materials of deep mining minerals and imposing that they must be processed first in the country.

One type of minerals that has not been explored is zircon (Zr), whose form in zirconia (ZrO_2) is abundant in Sumatera and Bangka Island. Research on zirconia (ZrO_2) coming from natural resources has been widely carried out, but the number is still minimal compared to the number of research on technical or commercial zircon from companies. Based on the results of XRF, the zircon (Zr) content in Central Kalimantan especially in Kereng Pangi area reaches 70%, which is greater than the average of other zircon sand which reaches only around 60%.[1] Thus, is very potential to be explored considering that zirconia (ZrO_2) has many advantages including the electrical and thermal conductivity as well as very low thermal expansion, the high melting point, high hardness and toughness, and better

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performance than other types of ceramics. Moreover, zirconia (ZrO_2) is widely used in numerous areas from the electronics world, automotive, oxygen sensors, fuel cell coatings to extreme applications such as nuclear reactor furnace coatings.

The synthesis process for extracting zirconia from natural zircon sand is greatly influenced by the synthesis method and heat treatment carried out, so most of the research has focused on these two aspects. Variations and trials against parameters of both aspects are widely used to get the best results. One of the methods that is widely developed is alkaline fusion-coprecipitation. This method requires a temperature that is not too high, and the process is simple, so it supports the aspects of efficiency and effectiveness if applied in the industrialization. The alkaline fusion-coprecipitation method consists of two main components, which are zircon sand melting with alkaline materials leaching which also consists of two stages, namely water leaching and acid leaching, followed by coprecipitation. In the coprecipitation process, the effect of pH and precipitation calcination temperature which is formed from natural material has not been widely reported when compared to the effect formed from technical materials.[2]

The synthesis process of ZrO_2 with alkali fusion method using alkaline NaOH materials has been reported to be carried out by BATAN. In addition, a combination of NaOH and KOH from natural zircon sand of Bangladesh has also been conducted by Biswas. However, alkali fusion method with alkaline KOH has never been reported before. Therefore, this research will fill this gab and focus on the synthesis process of ZrO_2 from natural zircon sand of Kereng Pangi with alkaline KOH.[3]

Zirconia (ZrO2) is a polymorphic material with 3 different phases, namely monoclinic (<1170 ºC), tetragonal (1170 ºC – 2340 ºC) and cubic (> 2340 ºC). This phase change becomes a problem in applications with a high temperature range, so many studies have been carried out to obtain the phases in a stable form over their stable temperature range. Research on the behavior of ZrO_2 phase change (transformation) is intensively carried out to obtain stable phase of ZrO_2 that supports its application. One technique that has been widely developed is by doping ZrO_2 with divalent or trivalent cations like Mg^{2+} ,Ca^{2+}, Y^{3+},Sc^{3+} to obtain a stable phase at room and high temperatures.[4] This present research focusing on natural zircon sand with pH and calcinations has never been done before.

Methods

Natural zircon sand from Kereng Pangi of Central Kalimantan analyzed by XRF and XRD to observe the elemental content of Zircon and its compound form in the form of $ZrSiO_4$ followed by a magnetic separation process to reduce magnetic impurities. Moreover, the reduction of the size of zircon sand was carried out until a size of 100 mesh was obtained, and then is was washed using an ultrasonic cleaner to clean the surface of the particles.

The melting process was later carried out with a mole ratio of zircon sand: KOH of 1: 4 at a temperature of 700 ºC for 3 hours. The result of smelting namely “frit” was then continued to be washed using aqua dest 3 times for one hour of steering at a rotating speed of 160 rpm to remove any unreacted KOH residues. Following this, the melted product was dried and then leached with 10% HCl for one hour at a stearer speed of 160 rpm with a ratio of 1 gram of frit to 30 ml of 10% HCl. the solution was filtered to take the filtrate. The filtrate was later precipitated with NH_4OH at pH 4, 7 and 10 overnights. In the stage that follows, the precipitation was dried and then tested for DTA TGA to determine the temperature of calcination. Eventually, the results of calcination were tested by XRD and XRF to determine the characteristics of the sample.

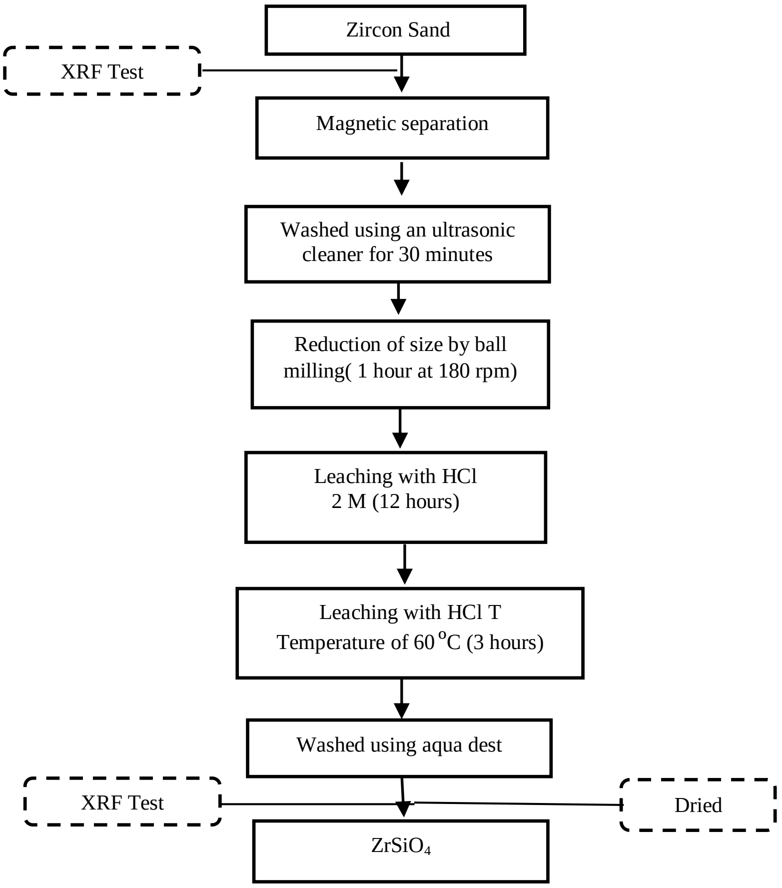


Figure 1. Flow Chart of Zircon Sand ($ZrSiO_4$) Purification

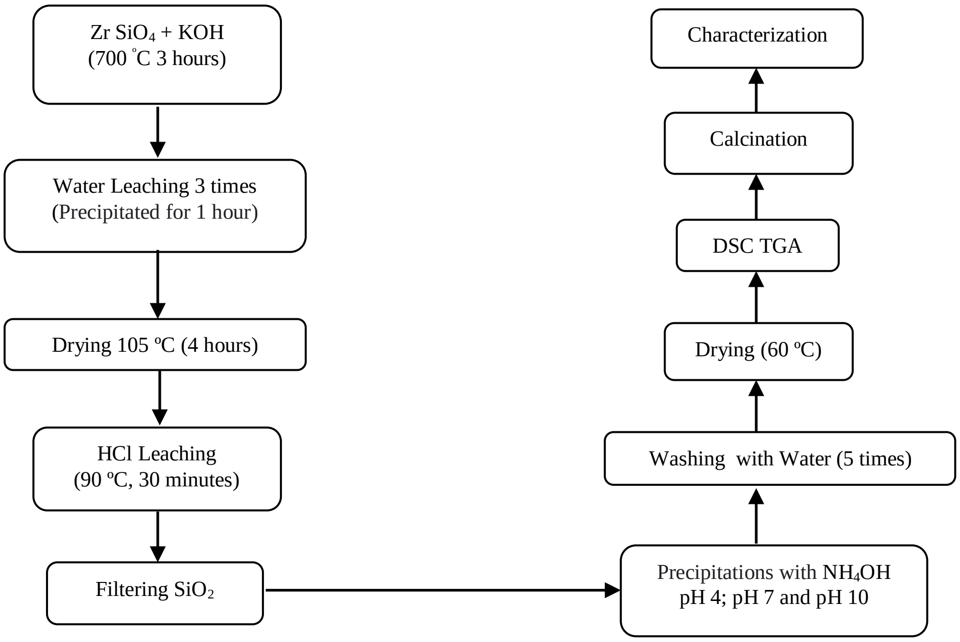


Figure 2. Flowchart of the Synthesis of ZrO_2 from Zircon Sand ($ZrSiO_4$)

Results and Discussion

The results of XRD and XRF for natural zircon sand of Kereng Pangi as an initial identification of the elements contain an indication of their potential feasibility for the extraction process. From the XRF results in Table 1, it is shown that zircon (Zr) content is quite large, reaching 70% in the form of $ZrSiO_4$ in nature. The results of the synthesis of Zirconia (ZrO_2) of 86% were later be analyzed for the effect of pH and temperature calcination.

Smelting with alkaline materials for KOH produces different results from NaOH. Specifically, in the alkaline NaOH material, the same conditions including the temperature of 700 ºC (for 3 hours) and the comparison between 1: 4 mole ratio are able to break the ZrO_2 and SiO_2 bonds in the $ZrSiO_4$ compound by reaction:

$$ZrSiO_4 + 4\,NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O$$

$$ZrSiO_4 + 2\,KOH \rightarrow K_2ZrSiO_5 + H_2O$$

NaOH is able to break down ZrO_2 and SiO_2 while KOH is not able to break it down, but it reacts to form K_2ZrSiO_5 which is more reactive with HCl.[5]

Table.1 Data on XRF results at each purification stage (A) initial conditions, (B) after magnetic Separation (C) leaching with HCl at 600 ºC for 3 Hours (D) leaching with HCl at 600 ºC for 6 Hours, and (D) $ZrSiO_4$ purification results by the factory

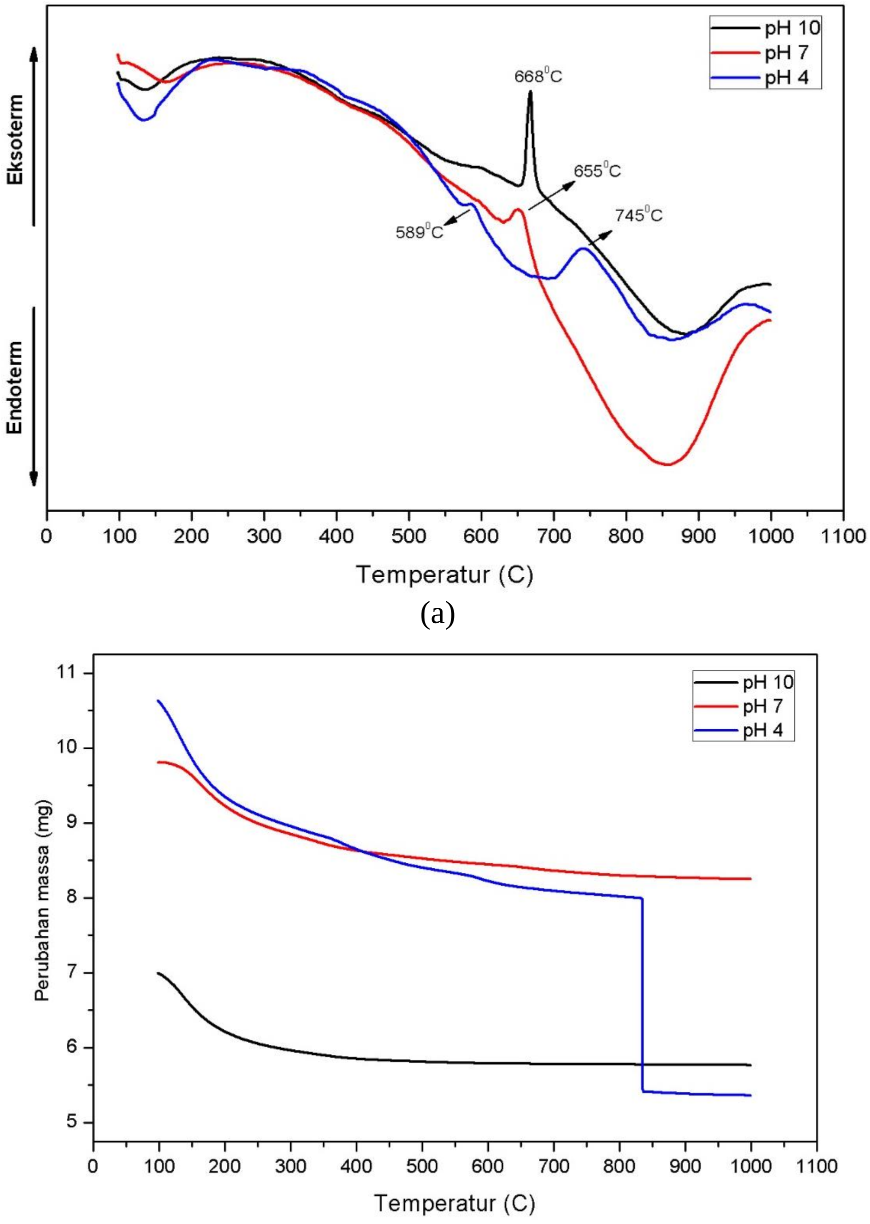
Element	Weight Percent (%)				
	A	B	C	D	E
Zr	70.40	90.90	95.20	95.30	95.80
Ti	19.40	3.59	1.29	1.30	0.54
Fe	6.34	0.27	0.099	0.077	0.09
Hf	1.23	1.27	1.41	1.36	1.42
Si	0.50	2.99	1.00	1.00	0.84

From Table 1, it is shown that the magnetic separation process is very good for reducing magnetic impurities, especially Fe impurity elements. In addition, the zircon sand has a lighter color than the color before the magnetic separation, which is dark due to the presence of impurities which contain a lot of Fe and Ti. Then, the zircon sand was washed with an ultrasonic cleaner to clean the surface and dried.

The Zr(OH)4 powder from the synthesis results was analysed by DTA-TGA to determine thermal characteristics and calcination temperature in forming the zirconia phase. The DTA-TGA result process was carried out with a rise in temperature of 100 ºC / minute. The DTA-TGA results are shown in Figure 3.

The DTA results at each pH show a similar pattern from 0 ºC to 500 ºC where an endothermic reaction occurs, followed by a mass decrease in TGA. It indicates that the heat energy in the sample is absorbed as latent heat to evaporate the hydrate element at Zr(OH)4 to ZrO2 by vaporizing the hydroxyl (OH-) bond group. In addition to evaporating OH-, it also evaporates the remains of H+ ions and the remaining salts from the side reaction.[6]

The exothermic peak reaction in the sample with a depositional pH 10 and pH 7 occurs at a temperature of 668 ºC and 655 ºC, and for pH 4 there are two peaks at 589 ºC and 745 ºC. This reaction is a reaction to form ZrO_2 crystals in a tetragonal phase. Moreover, the TGA chart starts to be constant at pH 10, pH 7 and pH 4 starting at temperatures of around 650 ºC, 707 ºC and 750 ºC. The TGA graph at pH 4 falls at a temperature of 834,5 ºC, so it is possible that mass overflow occurs because of the use of $Zr(OH)_4$ mass that is too large.[7]



(a)

(b)

Figure 3. Results of DTA-TGA of $Zr(OH)_4$ synthesized from natural zircon sand of Kereng Pangi (a) DTA (b) TGA.

Based on the results of DTA-TGA analysed, calcinations were carried out at temperature variations of 550 ºC, 600 ºC, 650 ºC and 700 ºC with a holding time for 3 hours. The XRD results are shown in Figure 4.

XRD analysis results for all depositional pH show that the higher calcination temperature, the higher the degree of crystallinity of ZrO_2, specifically in the increase in crystal size formed. The crystal size of ZrO_2 is also influenced by pH precipitation; with an increase of pH precipitation, it makes crystal size smaller. The size of crystallinity and the largest number of crystalline fields are formed at acidic depositional pH and vice versa, while the smallest crystal size is formed at alkaline depositional pH.

ZrO_2 resulting from alkaline deposition (pH 10) still has an amorphous structure at a temperature of 550 ºC, while at acidic and neutral pH, tetragonal ZrO_2 crystals have been formed, indicating that the crystallization process at pH 10 is much slower than the crystallization process at other pH. This difference is possible because the deposition process at pH 10 is much faster than that other pH, so it produces more random gel structure than the acidic and neutral pH gel structure do, which makes it more difficult to form crystals. $Zr(OH)_4$ gel at depositional pH 10 is dispersive and soft, characterized by water filtering which is easier to penetrate the gel. In this present study, there are 5 crystal fields identified, namely (011), (110), (020), (121) and (202).[8]

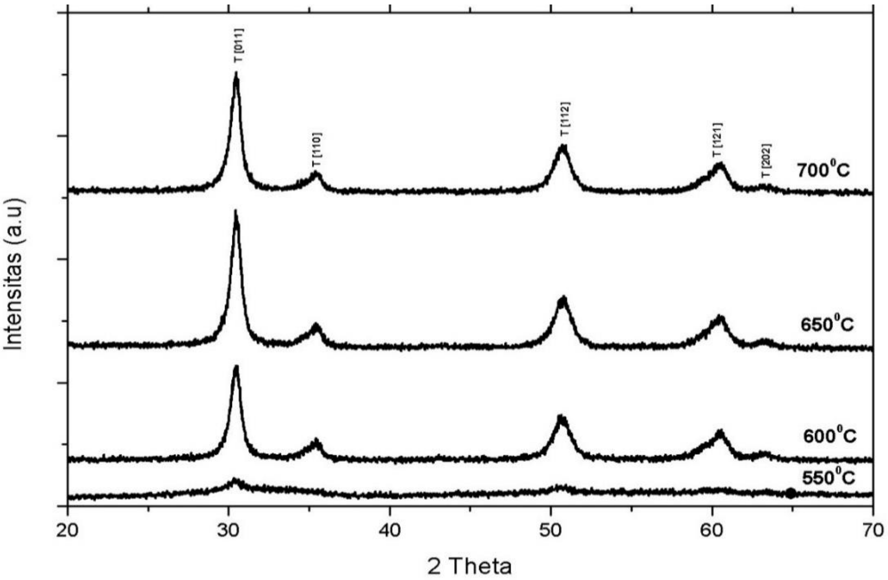


Figure 4. XRD results of synthesis of ZrO_2 from natural zircon sand of Kereng Pangi for precipitation atin pH 10.

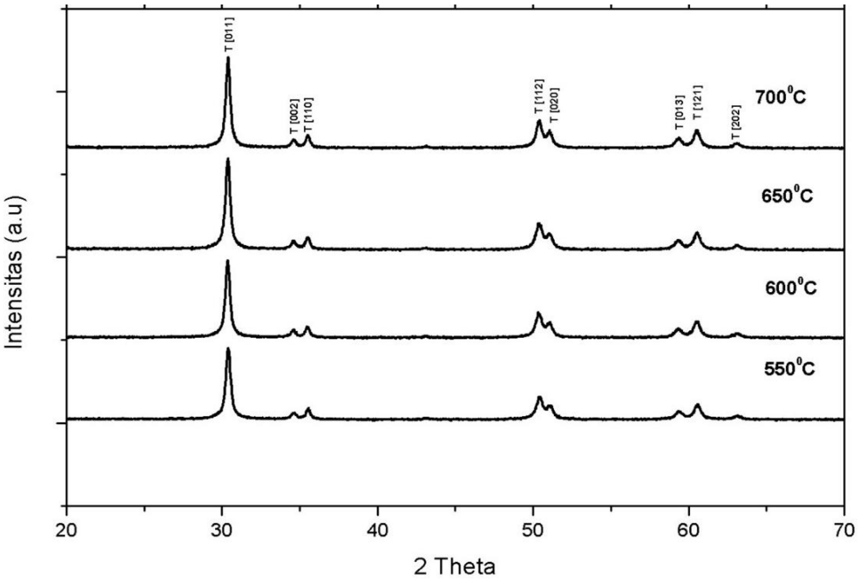


Figure 5. XRD results of synthesis of ZrO_2 from natural zircon sand of Kereng Pangi at (a) neutral depositional pH (pH 7) and (b) acidic depositional pH (pH 4)

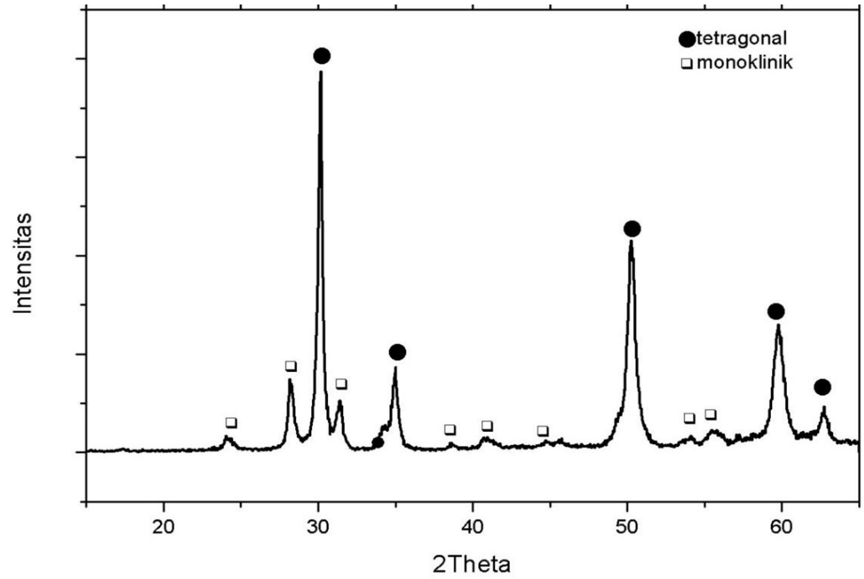


Figure 6. XRD results for ZrO_2 Aldric technical products (commercial)

The same condition also occurs at pH 7, but the number of crystalline fields formed is more at than pH 10 with 7 crystal fields, namely (011), (002), (110), (020), (112), (013), (121). Moreover, (202) is also possible because the precipitation rate at neutral pH is not as fast as at pH 10, so the $Zr(OH)_4$ regularity is better than the regularity at pH 10 are.

XRD results also show the crystallinity of ZrO_2 at acidic pH (pH 4) is higher than that at neutral (pH 7) and alkaline (pH 10). This is because at pH 4 the precipitation rate is very slow compared to the rate at other pH as it takes about 12 hours (overnight). The result is the structure of $Zr(OH)_4$ gel which is formed more regularly, marked by a clumpy gel condition due to a coagulation process in the gel, whith forms a stronger bond, marked with water on the gel. Thus, it is more difficult to penetrate the gel and filter paper compared to pH 7 and 10. Therefore, pH 4 is much easier to form crystal structures than pH 7 and 10.

The number of crystalline fields formed is at most 8 crystal planes, namely (011), (002), (110), (112), (020), (013), (121) and (202). When compared with the commercial ZrO2 Aldric product, Figure 5. shows that commercial ZrO2 consists of two phases, namely the tetragonal and monoclinic phases. The monoclinic phase has appeared, so only the recalcination process is needed. Furthermore, the transformation process will occur from a tetragonal to monoclinic phase and at the end, one monoclinic stable phase will be obtained.[3]

The XRD results analysis combined with MAUD calculation result at a temperature of 550 ºC, which indicates that pH 4 has a crystal size greater than pH 7 and pH 10 do. The exothermic peak of pH 10 at 688 ºC (DTA-TGA figure) has a high exothermic peak only due to the total crystallization process. Meanwhile, the exothermic peak of pH 7 at 655 ºC and pH 4 at 589 ºC is smaller due to not only the crystallization process but also the evaporation process, which is marked by the process of decreasing mass on the TGA graph at around that temperature.

Garvie reported that the maximum crystal size of tetragonal ZrO_2 phase before transforming into the monoclinic phase is 30 nm. However, the ZrO_2 synthesized from natural zircon sand of Kereng Pangi produces a tetragonal phase that can survive even though the crystal size is more than 30 nm. Moreover, the impurity factor inhibits tetragonal to monoclinic phase transformation process. The tetragonal phase is formed to be a metastable phase because it is susceptible to temperature, pressure, crystal size and depositional pH which can withstand the temperature and crystal size ranges of commercial technical precursors that have been reported by previous researchers.[9]

Table 2. Results of the calculation of the crystal size of ZrO_2 synthesized using MAUD software

Calcination Temperature	Crystal size (nm)		
	pH 4	**pH 7**	**pH 10**
550ºC	101	44	8
600ºC	102	47	42
650ºC	104	54	47
700ºC	110	66	48

Table 3. PSA results of synthesized ZrO_2 from natural zircon sand of Kereng Pangi

Calcination Temperature	Crystal Size (nm)		
	pH 4	**pH 7**	**pH 10**
550ºC	255	301	227
600ºC	238	243	261
650ºC	251	248	262
700ºC	292	261	264

The results of PSA analysis show that the particle size is getting bigger with the increasing temperature. The relationship between particle size and pH settling is still very different from the relationship between pH and crystal size as a result of MAUD software analysis. Particles are a combination of several crystals, and the relative particle size increases with the increasing temperature. However, for the comparison of particle size with pH, a relationship cannot be drawn, in contrast to MAUD analysis showing that a higher pH precipitation results in a smaller crystal size. This is possible because of the large agglomeration of zirconia samples due to a lack of deposition time or the type of dispersant in the form of soap to disperse the ZrO_2 particles, so it is less effective at dispersing the ZrO_2 trenches. The smaller particle size tendency for agglomeration to occur is greater because it has a larger active outer surface. The atoms on this surface have an incomplete coordination site (dangling bond), so the surface atoms will fill each other with the empty coordination site to form agglomerations.[10]

The results of XRF analysis in Table 4. show that ZrO_2 levels at pH 4 are around 98.5%, slightly smaller than those at pH 7 and pH 10 at around 96.3%. This is possible because the mass of $Zr(OH)_4$ or ZrO_2 is less, so the percentage decreases slightly. This happens because at pH of acidic precipitation, the quantity of OH^- ions from the addition of NH_4OH is less than that in neutral or alkaline conditions. The presence of H^+ ions in acidic conditions also reduces the rate of precipitation process because H^+ ions also bind OH^- ions to form water thereby reducing the concentration of OH^- ions to precipitate Zr^{4+} from $ZrOCl_2$ to form $Zr(OH)_4$. On the contrary, in neutral or alkaline conditions, H^+ ions as a measure of acidic pH do not exist, and the abundant OH^- ion concentration makes OH^- bonds at each corner of the Zr^{4+} bonds, so all Zr^{4+} ions bind perfectly to OH^- and precipitate at a fast precipitation rate.[6]

The amount of OH^- ion concentration greatly affects the quantity of Zr^{4+} deposition in the form of $Zr(OH)_4$ gel. The result is that the mass of $Zr(OH)_4$ and ZrO_2 at alkaline pH (pH 10) is greater than that in the the neutral and acidic pH. The mass of $Zr(OH)_4$ is directly proportional to the mass of ZrO_2 with a mass reduction of 20-30% after the calcination process. The mass of ZrO_2 resulting from pH 4 is relatively smaller, so the concentration decreases compared to the mass of impurities and vice versa. This is the reason why the ZrO_2 level at the pH of the depositional pH (pH 4) is relatively smaller than that at the neutral pH (pH 7) and alkaline (pH 10).

The purity level of synthesized ZrO_2 is known through XRF analysis as shown in Table 4. The results of XRF analysis show that ZrO_2 can only be produced with an average purity level of 96%. The lowest ZrO_2 level at pH 4 is possible because at pH 4 the concentration of NH_4OH as a precipitant is less than at pH 7 and pH 10, so the ZrO_2 concentration is less than that at pH 7 and pH 10. Another reason is that the distribution of impurities in Zircon sand is not possible. To be uniform.

Table 4. XRF results of synthesized ZrO_2 from natural zircon sand of Kereng Pangi

Element	**Weight percent (%)**		
	pH 4	**pH 7**	**pH 10**
ZrO_2	95.80	96.30	96.30
HfO_2	1.56	1.41	1.46
TiO_2	2.09	1.71	1.51
Fe_2O_3	0.12	0.10	0.08
SiO_2	-	-	-

Conclusion

From the research that has been done, it can be concluded that the synthesis of ZrO_2 from Kereng Pangi natural zircon sand using alkali fusion-coprecipitation method with alkali KOH has been successfully carried out. The results show that ZrO_2 level under acidic depositional pH conditions (pH 4) is 95.8%, while in neutral pH (pH 7) and alkaline (pH 10), the pH condition is 96.3%. The increase of pH precipitation has an effect in reducing crystal size of ZrO_2 formed with the largest crystal size at the calcination temperature of 700ºC, namely acidic depositional pH (pH 4) 110 nm, neutral depositional pH (pH 7) 66 nm and alkaline deposition pH (pH 10) 48 nm. The effect of pH precipitation variations in acidic (pH 4), neutral (pH 7) and alkaline (pH 10) conditions with a calcination temperature ranging of 550 ºC to 700 ºC has not yet formed a ZrO_2 monoclinic phase. The ZrO_2 phase formed is a tetragonal single phase, which is stable up to the temperature of 700 ºC

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