03. Optimizing zircon powder synthesis by varying zircon sand mass to HCl moiarity ratio

by Nur Aini Fauziyah

Optimization of Zircon ($ZrSiO_4$) Powder Synthesis by Varying Zircon Sand Mass to HCl Molarity Ratio

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Abstract. Zircon powder ($ZrSiO_4$) was successfully synthesized through variation of puya sand mass and reduction of HCl molarity. The aim of this study is to produce zircon powder in large quantities with more efficient time. Puya sand was obtained from Kereng Pangi, Central Kalimantan, Indonesia. Zircon powder was synthesized through the process of mesh 40 sieves, magnetic separation, ball milling, and HCl immersion. This study used 2 types of sand namely P1_0 (Puya sand 1) and P2_0 (Puya sand 2) with a mass variation of 30, 40, 50, and 60 g and HCl molarity used is 0.5 M. X-Ray Diffraction (XRD) characterization was used to identify phases formed in zircon powder. While X-Ray Fluorescence (XRF) characterization is used to know the composition of zircon powder. Results showed, P1_0 with all mass variations have the zircon content of 100 wt % (zircon productivity increased by 100 % than initial mass). Meanwhile, the P2_0 with a mass of zircon sand 40 g has the highest zircon content of 89.84%. Thus, zircon productivity P2_0 increase by 65% than initial mass.

Introduction

Indonesia is a country with a large supply of zircon sand especially in Central Kalimantan[1]. Zircon sand in the Central Kalimantan River (watershed) area reached 6,556 million tons which has a silicate zirconium ($ZrSiO_4$) content of 2,615 million tons [2]. It is residual from gold waste or from zircon sand mining (puya sand). The zirconium oxide, metallic zirconium and other materials production can be obtained from zircon [3]. Zircon is a common mineral scattered in a wide variety of rocks such as sedimentary, igneous, and metamorphic rocks [4]. Zircon ($ZrSiO_4$) is formed from silica (SiO_2) and zirconia (ZrO_2) stoichiometric reactions or $ZrO_2.SiO_2$ [5]. It is an important ceramic material with many advantages, such as good thermal and chemical stability, high mechanical strength at high temperature [6]. Moreover, zircon ceramics have well physical and chemical properties for technology. The properties of zircon are: high hardness grade (7.5 Mohs), low thermal expansion ($4x10^{-6}$ °C^{-1} in the range 25-1400°C) and a high dissociation temperature (1675 °C) [7]–[9]. The density of puya sand is 4.68 g/cm^3. The color of the puya sand is

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varied such as yellowish, pink, reddish, brownish, colorless, and sometimes green, blue or black [10]. Especially colorless zircon is sometimes used as alternative for diamond [11]. However, the puya sand obtained from the nature has several unnecessary impurities. Because of this, to obtain pure zircon powder, a complicated method is necessary [1]. Therefore, efforts to process zircon sand into functional materials, especially with simple technology, need to be done to increase economic and functional added value for it. One way to produce zircon powder is a purified the zircon sand (puya sand). Zircon powder was synthesized through the process of mesh 40 sieves, magnetic separation, ball milling, and HCl immersion. Musyarofah has succeeded in producing a pure zircon powder from puya sand but the zircon purification used relatively high concentrations HCl of 2 M and heating at 100 °C [1]. In a previous study, Amalia had purified zircon sand from puya sand. It showed the effectiveness of HCl in reducing impurities contained in the puya sand was obtained by combining the HCl concentration of 0,5 M and heating temperature of 80°C [12]. However, the process to obtain pure zircon from the synthesis of zircon sand takes a long time. While the results of zircon powder obtained are still (30 g mass of raw material obtained 28 g zircon powder). In this study, we will optimize the synthesis process of zircon powder from puya sand through variation of puya sand mass with molarity and fixed temperature. Optimization of mass and molarity ratio is expected to reduce HCl. The excessive use of HCl concentration will have a negative impact on the environment and health, and needs higher costs. In other words, researcher is expected to produce high purity zircon powder in large quantities of zircon with more efficient time.

Method

Preparation of samples

The raw material (Puya sand) type P1_0 and P2_0 taken from Kereng Pangi, Central Kalimantan, Indonesia. The purification was carried out in four main processes, i.e., sieved, magnetic separation, ball milling, and immersion in HCl. Puya sand was sieved using a siever with a mesh size of 40. The magnetic separation process, using a permanent magnet, aimed to removed magnetic impurities compounds (Fe) in the sand. After that, the milling process was performed using a planetary ball milling for 2 hours at 150 rpm. Then the sand (30 g, 40g, 50g, 60g) was immersed to HCl with concentrations 0.5 M at 80 °C for an hour to separate the impurities (Ti). The mixture was allowed to stand for 24 hours to obtain a precipitate and then washed it with aquades to get a netral pH. The notations of sample was used in this research shown in table 1.

Table 1. Nomenclature of samples.

Samples	Description
P 1_0, P2_0	Raw materials (Puya sand) from two locations (P1 and P2)
P1_40, P2_40	Puya sand after sieved by using 40 mesh
P1_40S, P2_40S	Puya sand after sieved by using 40 mesh and magnetic separation
P1_30H, P1_40H, P1_50H, P1_60H, P2_30H, P2_40H, P2_50H, P2_60H	Puya sand, after sieved by using 40 mesh and magnetic separation, was immersed in HCL with variations of mass (30 g, 40g, 50g, 60g).

Characterization

X-Ray fluorescence (XRF) characterization were applied for the elemental content of samples. The X-Ray diffraction (XRD) pattern were carried out by X-Ray Diffractometer (λ CuKa=1.54056 Å) for all samples with step size of 0.0170°. Match!2 software was used to identify the phase and using Rietica softwares based on Rietveld method to provide accurate phase compositions of the samples.

Result and Discussion

The results of XRF and XRD characterizations of the samples in each purification process, i.e., raw materials (P1_0, P2_0), after sieved mesh of 40, and puya sand (sieved) after magnetic separation and milling process are shown in Table 2 and Figure 1. X-ray fluorescence analysis shows the zircon sand contained of zirconium, silicon, titanium, iron, and hafnium in. XRF data shows that the magnetic separation process of P1_0 and P2_0 after sieved with permanent magnets can remove Fe and decrease some quantity of Ti. Elements Fe and Ti are decrease because during the magnetic separation process, they are attached to the magnetic stem. Meanwhile, qualitative analysis of the X-ray diffraction data revealed that zircon ($ZrSiO_4$, PDF 00-006-0266), quartz (SiO_2, PDF 00-085-0798) exist in the sand. Meanwhile, in addition to the both phases, sand type P2 contains CaO phase.

Table 2. XRF elemental content (wt%) of the raw materials (P1_0/P2_0), after sieved mesh of 40, and the sand (sieved) after magnetic separation (40S)

Samples	Zr	Si	Ti	Fe	Hf
P1_0	83.49	6.00	6.32	0.89	1.95
P1_40	81.12	12.78	3.47	0.43	1.39
P1_40S	82.39	12.47	2.81	-	1.29
P2_0	70.00	9.82	14.30	2.71	1.59
P2_40	59.79	20.05	15.48	2.96	0.93
P2_40S	66.14	23.2	9.35	0.11	1.18

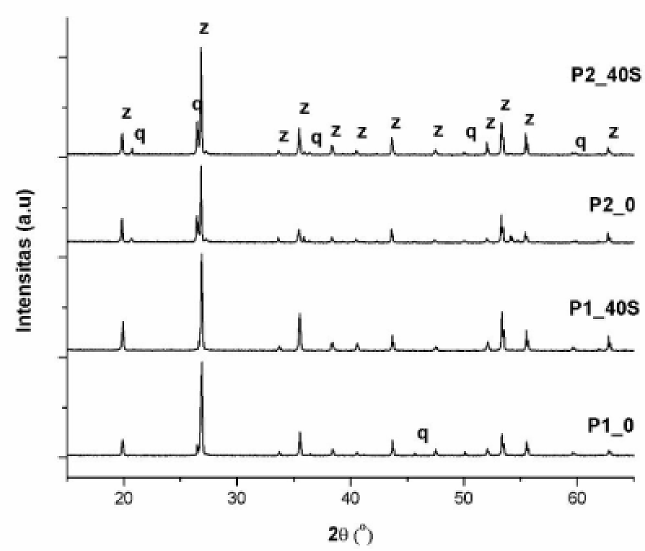

Fig. 1. X-ray diffraction patterns (CuK α radiation) of P1_0, P2_0 after sieved mesh of 40 and P1_40S, P2_40S. Symbols: z = zircon ($ZrSiO_4$), q = quartz (SiO_2).

Table 3 shows the composition of P1_0 and P2_0. The zircon composition of P1_0 is more dominant than that (P2_0). Meanwhile, after the magnet separation process, composition of the zircon phase P1_0 decrease, but the composition of the phase quartz increased up to ~28.2 wt%. Conversely, after magnetic separation, the composition of the quartz phase P2_0 reduced to ~14 wt% due to the magnetic elements (i.e. Fe) reduced, while elements of silica (quarz) can not be attracted by magnets during the process of magnetic separation, resulting in the content of quartz increase. This result is the same as that done by Musyarofah, where the quartz phase is increase after magnetic separation process [1].

Figure 2 (a) and (b) show XRD patterns samples of zircon powder after immersed in HCL with codes (30, 40,50, 60) for variations in puya sand mass (g) and H for the synthesis of HCl. Qualitative analysis that shows the dominant phase contained in P1_0 after the synthesis of HCl is zircon (PDF 00-083-1374). While in addition to the zircon phase, P2_0 contains quartz (PDF 00-085-0797). We used Rietica to analysis the phase of sample where the result can be seen in Table 4.

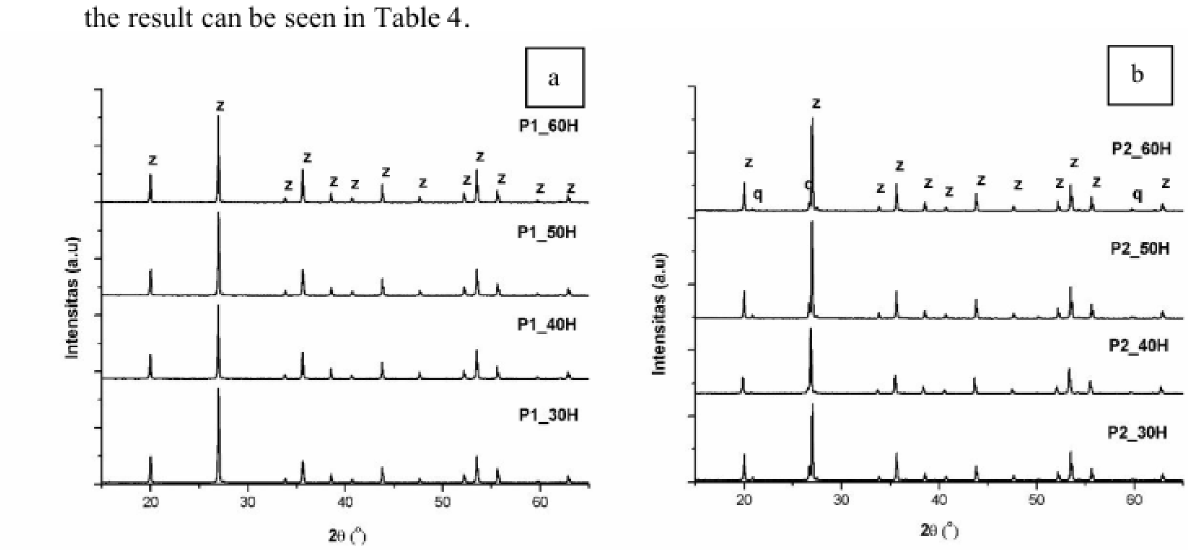

Figure 2. X-ray diffraction patterns (CuKα radiation) of zircon powder after immersed in HCl (A) puya sand type P1 (B) puya sand type P2 Symbols: z = zircon ($ZrSiO_4$), q = quartz (SiO_2).

Table 3. Phase composition (relative weight fractions) using Rietica software the puya sand and the sand after magnetic separation

Samples	Phase	Wt (%)	R_{Bragg}	GoF
P1_0	$ZrSiO_4$	98(2)	6.3	3.1
	Q-SiO_2	1(0)	6.1	
P1_40S	$ZrSiO_4$	69(4)	5.0	3.0
	Q-SiO_2	30(6)	2.7	
P2_0	$ZrSiO_4$	59(2)	7.6	4.0
	Q-SiO_2	40(3)	6.3	
P2_40S	$ZrSiO_4$	73(1)	7.0	3.5
	Q-SiO_2	25(1)	5.8	
	CaO	1(0)	9.7	

Table 4. shown P1 with mass variation has a single phase, namely zircon. Meanwhile, P2 with the same variation has zircon and quartz phases, as indicated in the results of qualitative analysis. Quantitative analysis confirms that the composition of the phase P1

shows 100% zircon, in contrast to P2 which has zircon composition in the range of 82%-89%.

Table 4. Phase composition (relative weight fractions) the puya sand after sieved mesh of 40 (40S) and the sand (40S) after magnetic separation (MS)

Samples	Phase	Wt (%)	R_{Bragg}	GoF
P1_30H	$ZrSiO_4$	100(0)	3.2	2.8
P1_40H	$ZrSiO_4$	100(0)	5.0	4.0
P1_50H	$ZrSiO_4$	100(0)	4.0	3.2
P1_60H	$ZrSiO_4$	100(0)	4.8	3.9
P2_30H	$ZrSiO_4$	82(1)	4.6	3.4
	Q-SiO_2	17(1)	3.0	
P2_40H	$ZrSiO_4$	89(1)	6.3	3.0
	Q-SiO_2	10(1)	3.2	
P2_50H	$ZrSiO_4$	83(1)	4.2	3.9
	Q-SiO_2	16(1)	2.7	
P2_60H	$ZrSiO_4$	88(2)	5.0	3.9
	Q-SiO_2	11(1)	1.8	

The composition of the elements of Si P1 after the magnet separation process with XRF test is 12.47 wt%, while Ti element composition is 2.81 wt%. Meanwhile, the composition of the P1 phase with using rietica software shows formed Zircon phase ($ZrSiO_4$) 100% shown Table 4. With thus, after the synthesis of HCl, the titanium element (Ti) P1 has been lost so that only obtained 1 phase, namely zircon. Furthermore, P2 has 2 phases compositions, namely zircon ($ZrSiO_4$) and quartz (SiO_2). Puya sand type 2 after magnetic separation titanium (Ti) content of 9.35 wt%. While the silicon element (Si) after magnetic separation indicates 23.2 wt%. HCl synthesis process successfully eliminates elements titanium (Ti), but not with silicone elements (Si) as reported by Amalia [12]. HCl synthesis process eliminate the element Ti, because the titanium element (Ti) can be bound by HCl.

Conclusions

The high-purity zircon has been successfully synthesis from puya sand as the raw material through variation of puya sand mass and reduction of HCl molarity. Reduction of HCl molarity 0.5M and processing temperature at 80°C remains effective in producing elements of zirconium (Zr) and phase zircons in large quantities. Sand type P0_1 with all mass variations has 100 wt% zircon content, so zircon productivity increases by 100%. The highest zircon content in P0_2 is 89.84 wt% and occurs in zircon sand mass of 40 gr. In the other words, zircon productivity in P0_2 increased by 65%.

Acknowledgement

The authors acknowledge the financial support from Kemenristek/BRIN through World Class Research 2020 granted to SP.

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