

SIZE VARIATIONS OF ZIRCON SAND IN SYNTHESIS ZIRCONIA USING ALKALI FUSION - COPRECIPITATION METHOD

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Abstract

This paper aims to analyze the effect of size variation of zircon sand in synthesis zirconia (ZrO_2) using Alkali Fusion – Coprecipitation method. Zirconia is a refractory ceramics materials which has good properties of polymorphs, high density, high hardness, and low heat conductivity properties. In this work, zirconia is obtained from the synthesis of natural zircon sand. Synthesis begins with the separation of magnetic element used magnets, then it was washed. The dried sand were crushed and sieved with a sieve 100 mesh, 200 mesh and 325 mesh respectively. The each sample were mixed with KOH and heating in electrical furnace at temperature 700°C for 3 hours. After that it was washed by water and were dried. The samples were reacted with HCl then were filtered using filter paper. The filtrate were reacted with NH_4OH to reached PH 10 for each sample then were precipitated for 12 hours. The results were dried using an oven. After dried, the sample were calcined at temperature 800°C for 5 hours. The amorphous structure zirconia was formed in 100 mesh but the crystal structure zirconia was formed in 200 mesh and 325 mesh with estimation of crystal size is 5,21 nm and 5,54 nm respectively. The crystal structure zirconia is single phase in tetragonal with space group P 42 / n m c.

Key words: Zircon sand, Zirconia, Alkali Fusion, Coprecipitation

INTRODUCTION

Zirconia (ZrO_2) is a refractory ceramic material which has good properties of polymorphs, high density, high hardness, and low heat conductivity properties [1]. In the other hand low neutron absorbance of zirconia make it will be the strategic materials in nuclear industry. Development of technology based zirconia rapidly make the need consumption of zirconia increased [2].

The unstable crystalline of zirconia make it rare to find ZrO_2 pure in nature. Mostly it found mixed with other chemical elements such as silica and formed zircon (ZrSiO_4). In nature, zircon was found in sand which occupies about 25 % of the earth crust, make it will be the main raw of zirconia [3]. Zircon is the stable material ($G^\circ_{1400\text{K}} = 1489.1 \text{ kJ/mol}$) and decomposes at 1690°C in atmospheric pressure [4].

Crystal phase of polymorph zirconia was formed at 1170°C up to 2680°C [5]. Therefore it required precise and efficient method to synthesis zirconia from zircon. Alkali Fusion is usually method are used to decompose zircon with alkali as fluxing agent at $600^\circ\text{C} - 900^\circ\text{C}$ [6]. Reducing crystal size of zirconia using coprecipitation method where material was solved in to acid solution and will be precipitated by precipitating agent such as hydroxide, carbonate, sulfate, and oxalate

[7]. In this research will be analyze the effect of size variation of zircon sand in synthesis zirconia (ZrO_2) using Alkali Fusion – Coprecipitation method.

RESEARCH METHOD

The natural zircon sand from Kereng Pangi, Central Kalimantan were characterized by X-Ray Fluorescence (XRF) to determine the contents of elements from natural zircon sand before ready for preparation process. The preparation process began with separated sand from magnetic elements used magnet. After that, it was washed with water using an ultrasonic cleaner during 30 minutes in three times. The drying sand were grinded and sieved with a sieve 100 mesh, 200 mesh and 325 mesh respectively.

The each sample were mixed with KOH used ratio 1 gr sample : 1,5 gr KOH, and heating in electrical furnace at temperature 700°C for 3 hours. After that it was washed by water and repeat until three times then drying. The results of water leaching were reacted with HCl used ratio 1 gr : 30 mL HCl 10% then were filtered using filter paper. The filtrate were reacted with NH_4OH to reached PH 10 for each sample respectively then it was precipitated for 12 hours. The results of coprecipitation were dried using an oven and after dried, it was calcined at temperature 800°C for 5 hours. The final products were identified using XRD.

A qualitative analysis on identification for the crystalline phase was conducted using an X-Ray Philips X'Pert PRO in Research Center, LPPM ITS Surabaya, with software support of X'Pert HighScore Plus and Match! using database references of ICCD PDF2. Meanwhile, a quantitative analysis used software Rietica and MAUD.

RESULT AND DISCUSSION

The results of XRF identification of natural zircon sand from Kereng Pangi, Central Kalimantan are presented in Table. 1. which shows that the most dominant element is zirconium (Zr) with levels of 70.4%.

Table. 1. The results of XRF identification of natural zircon sand from Kereng Pangi, Central Kalimantan

Element	Percentage (% Wt)	Element	Percentage (% Wt)
Zr	70.40	V	0.44
Ti	19.40	Cr	0.43
Fe	6.34	Ca	0.27
Hf	1.23	Bi	0.13
Si	0.50	Ta	0.11
Mn	0.50	Pb	0.09

In nature, ZrO_2 was found in zircon sand so that it require separation and decomposition process. Separation process with magnet for separate impurity which have magnetic propertis such as ilmenite and tourmaline. After magnetic separation then were washed with water using an ultrasonic cleaner during 30 minutes in three times. The product of washing were dried and ready to identification of its elements using XRF.

The results of XRF identification and XRD spectra of preparation process was presented below:

Table. 2. The results of XRF identification after magnetic separation and washing process

Element	Percentage (% Wt)	Element	Percentage (% Wt)
Zr	90.90	Hf	1.27
Ti	3.59	Fe	0.28
Si	2.99	Ca	0.23

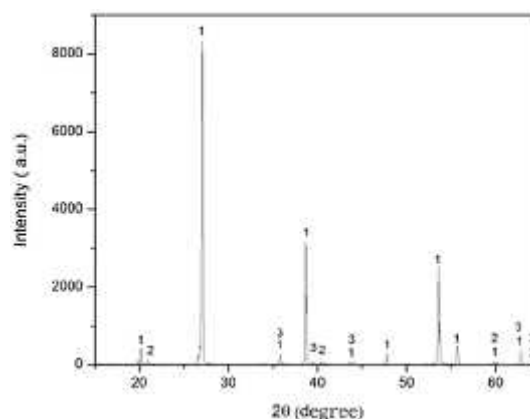


Fig. 1. The XRD spectra of ground zircon sample: 1-zircon (06-0266), 2-quartz (46-1045), and 3-rutile (21-1276). Figures in parentheses indicate the reference code number in the port of the XRD system used.

The percentage of Zr increase about 29% from initial after magnetic separation and washing process. It means that this method in preparation process is effective to reduces impurity especially Fe and Ti in the sands. The XRD spectra of it was showed in fig.1. Analysis using X'Pert HighScore Plus was obtained that the ground zircon we are used content quartz, rutile and zircon itself respectively. Mostly the high peak were identified is zircon peak and the others which small intensity is peak of quartz and rutile. Furthermore, ground zircon sand were crushed to obtain the precursor size are 100 mesh, 200 mesh and 325 mesh respectively. Standard size are used is Tyler Standard Designation. its refers to the distribution of the sieve holes on each length of wire which aperture sieve is calculated by calculating the difference between the distances of the sieve hole with a diameter of sieve wire. Details of the precursors size which are used was shown in the Table. 3.

Table. 3. Precursor size

Tyler Standart Designation				Sieve Standart Designation
Precursor (Mesh)	Number of slit /Inch	Distance of slit /Inch	Diameter of slit ($\times 10^{-3}$ Inch)	Precursor (Micron)
100	100	0,010	5,7	149
200	200	0,005	2,9	74
325	325	0,003	1,8	44

It is seen that the larger of mesh number have the smaller particle size. Particle size affects to cross-sectional area contact of material that can accelerate the rate of reaction. The smaller particle sizes of precursors make zircon that reacts with KOH when alkali fusion process increase. During alkali fusion process, bonding between Zr-Si are decomposed by fusion agent (KOH). Analysis using X'Pert HighScore Plus was obtained that compound were formed after alkali fusion process are Potassium zirconium silicate (K_2ZrSiO_4), Potassium zirconium oxide ($K_2Zr_2O_5$), and Zirconium titanium oxide ($ZrTiO_4$). There are some of zircon broke and formed Potassium zirconium oxide ($K_2Zr_2O_5$) and remaining formed K_2ZrSiO_4 and $ZrTiO_4$. After alkali fusion process sample leaching using water in three times. Based on XRD spectra and were analyzed, the kind of compound were formed are same with the result of alkali

fusion process. The intensity of sample after alkali fusion is lower than intensity of sample after water leaching process. It's indicated that crystallinity of sample after water leaching process increase. The background of sample after water leaching is smoother than background of sample after alkali fusion. It's indicated that in water leaching reduced some element or compound are soluble in water. The XRD spectra of it was showed in fig.2.

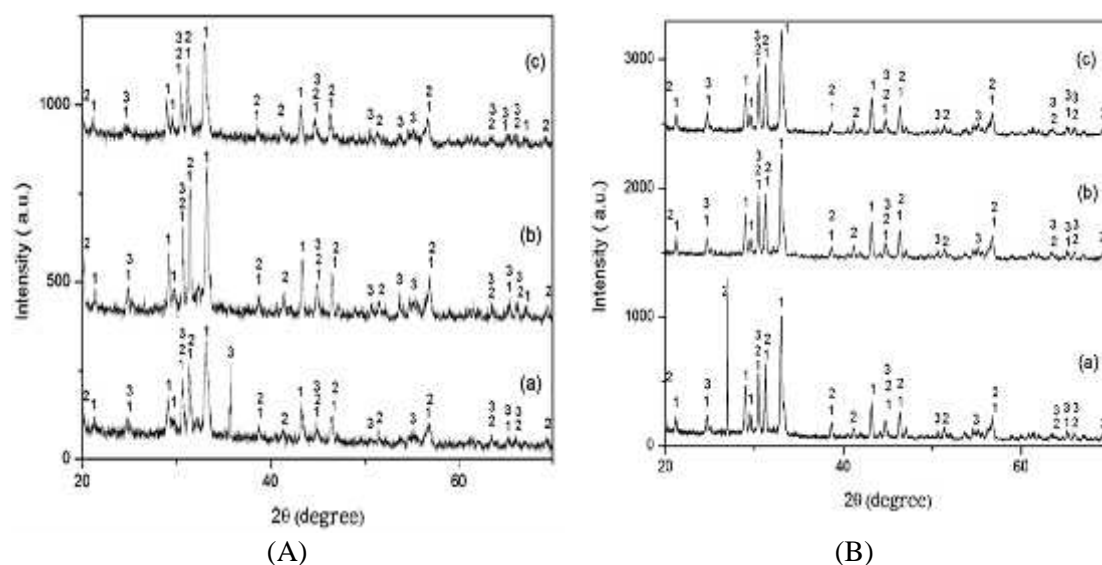


Fig. 2. The XRD spectra of sample after alkali fusion process (A) and after water leaching process (B): (a)-sample 100 mesh, (b)-sample 200 mesh, and (c)-sample 325 mesh. The number in figure shows: 1- K_2ZrSiO_4 (17-0282), 2- $\text{K}_2\text{Zr}_2\text{O}_5$ (20-0963), and 3- ZrTiO_4 (07-0290).

In sample 100 mesh appear significant peak at position 33° in XRD spectra after alkali fusion and not appear on the others. This peak is zirconium titanium oxide peak. It's indicated that in sample 100 mesh have content of titanium is more than the others. Sample 100 mesh have size bigger than the others, its possible for the smaller element were trapped inside. During alkali fusion process the element that were trapped inside not reacted with fusion agent so that the peak of zirconium titanium oxide appear significantly. However after water leaching process this peak vanish but appear the highest peak in XRD spectra at position 26.93° . This peak was indified as peak of potassium zirconium oxide. It's indicated that number of potassium zirconium oxide was increased after water leaching process. In the others this peak not appear exactly. Fig.3. show that losing mass from each sample after water leaching proses. The sample 325 mesh have the highest percentage of loss mass. The sample 325 mesh have smallest size so that it need more time to precipitate. The high amount of mass loss make the content of compound especially potassium zirconium oxide decrease. Different with sample 100 mesh that have biggest size it precipitated quicker than the others so that it have the lowest loss mass and amount of potassium zirconium oxide increase along with decrease of another compound. Deposition in water leaching process influence by earth gravity force that attract particles towards the center of the earth in this case the base glass. The smaller size of particles will get lower earth gravity force than the bigger size so that it need longer deposition time.

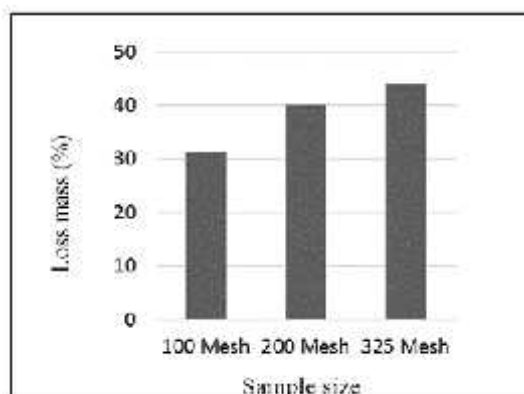


Fig. 3. The chart of loss mass in variation of sample size.

The XRD spectra of final product are shown fig.4. The Analytical results based on identification using software X'Pert HighScore Plus and Match! use database references of ICDD PDF2 was obtained that the XRD spectra of sample 200 mesh and 325 mesh are tetragonal zirconia with space group $P4_2/nm$. In sample 100 mesh has the lowest with large thus it can be concluded that it have an amorphous structure. This is caused by impurities phase formation that it can reduced temperature calcination. In calcination process, material absorb the heat to crystal growth and phase transformation. The heat are absorb by zirconia to crystal growth not fully but it absorb by impurities compound too, so that not enough energy for crystal growth.

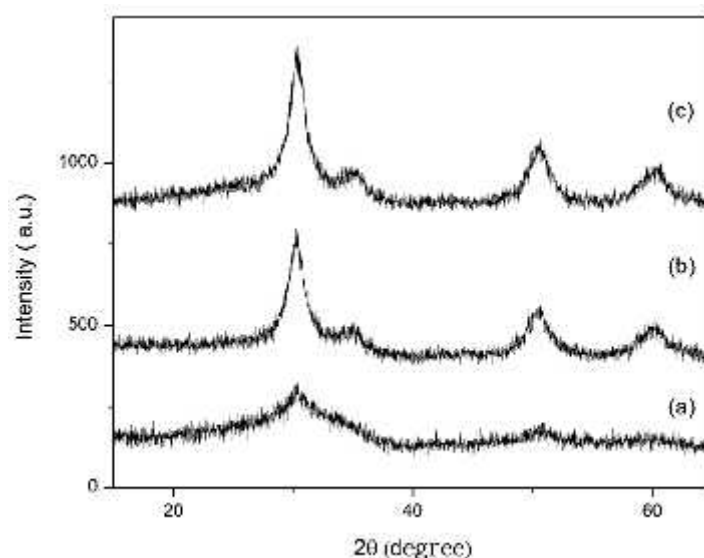


Fig. 2. The XRD spectra of final product: (a)-sample 100 mesh, (b)-sample 200 mesh, and (c)-sample 325 mesh.

On the size of 200 mesh and 325 mesh was formed crystal structure and have width peak are quite wide. The quantitative analysis used software Rietica and MAUD obtained results in Table.4. Structure of crystallinity for both sample is not much different. The tetragonal zirconia phase was formed at $1170^{\circ}\text{C} - 2370^{\circ}\text{C}$ but with alkali fusion - coprecipitation method it was formed at 800°C for 5 hours. Estimates of the crystal size is still relatively small about ± 5 nm.

Table. 4 Crystal parameters

Parameters		200 mesh	325 mesh
Lattice parameters(Å)	a	$3,556 \pm 0,004$	$3,558 \pm 0,004$
	b	$3,556 \pm 0,004$	$3,558 \pm 0,004$
	c	$5,084 \pm 0,009$	$5,067 \pm 0,007$
Density (g/Cm ³)		6,37	6,38
Crystal size (nanometer)		$5,21 \pm 2,68$	$5,54 \pm 2,84$
Microstrain		$0,021 \pm 0,001$	$0,019 \pm 0,001$

At grinding process sample get a tensile strain and compressive strain. When the calcination process the atoms get the relaxation condition where the strain has been released because it has enough energy to return to its initial position. It can be drawn from number of micro strain are relatively small in ranges ± 0.02 .

Tetragonal and cubic zirconia are zirconia structure which often used in industries based on zirconia. Both is unstable in room temperature so that should be stabilized. Stabilizing structure of zirconia generally used divalent cation such as Mg^{2+} and Ca^{2+} and trivalent cation such as Y^{3+} and Sc^{3+} which doped to the zirconia structure [8].

CONCLUSION AND SUGGESTION

Synthesis of zirconia from natural zircon sand with size variation of zircon sand using alkali fusion - coprecipitation method was done. In sample 100 mesh formed an amorphous structure. Meanwhile sample 200 mesh and 325 mesh formed crystals with estimates of crystal size are 5.21 nm and 5.54 nm. The smaller size particle cause the surface area of react increase. Beside it can make material more reactive, reduction of particle size in principle is to escape the compounds were trapped inside so that purification will be increase. Alkali fusion - coprecipitation method is efficient in synthesis zirconia from natural zircon sand. The Analytical results based on identification using software X'Pert HighScore Plus and Match! used database references of ICDD PDF2 was obtained that single phase tetragonal zirconia crystal structure with space group P 42 / n m c at 800°C for 5 hours.

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