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# THE EFFECT OF NAOH, KOH AND EQUIMOLAR MIXTURE OF NAOH AND KOH ON THE SYNTHESIS OF ZIRCONIA FROM INDONESIAN NATURAL ZIRCON SAND USING ALKALI FUSION METHOD

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**Abstract**

In this research, Indonesian natural zircon sand from Kereng Pangi, Central Kalimantan, was processed to determine the effect of NaOH, KOH and equimolar mixture of NaOH and KOH on the synthesis of zirconia using alkali fusion method. Synthesis of zirconia was started with initial preparation of zircon sand followed by alkali fusion with NaOH, KOH and equimolar mixture of NaOH and KOH. The fusion condition in this research was at 700 ° C for 3 hours with a zirkon:alkali wt. ratio of 1:4.8. The next step was leached with water, leached with HCl, precipitated with $NH_4OH$, and calcined at 500 °C for 3 hours. Fusing zircon sand with KOH was most favorable to get 99% zircon decomposition. The products were characterized trough X-ray diffraction (XRD). The zirconia that was resulted by fusing with KOH has a tetragonal structure as same as fusing with NaOH, whereas fusing with equimolar mixture of NaOH and KOH produces amorphous structure. Refinement results showed that tetragonal zirconia that was produced from fusion with NaOH has a similar lattice parameter and crystal size estimation values to fusion with KOH, it is mean that there was no significant effect of using KOH or NaOH on alkali fusion method to the lattice parameter and the crystal size of the resulting zirconia.

**Key words**: alkali fusion method, zirconia, zircon sand

## INTRODUCTION

The use of zirconia ($ZrO_2$) in various fields of technology for industrial applications has grown enormously. This is clearly related to its excellent mechanical, thermal, electrical, chemical and optical properties of zirconia [1]. Zirconia is commonly used in various applications such as catalysts, oxygen sensors, fuel cells, engine parts and thermal barrier coatings on metal surface [2].

Zirconia compound that found in nature cannot be directly used because it was mixed with other elements. In general, zirconia in nature is found in the form of zircon sand ($ZrSiO_4$) which is a natural combination of zirconia ($ZrO_2$) and silica ($SiO_2$) [3].

Synthesis of zirconia from zircon sand is not easy, because zircon is one of the most chemical stable compounds ($\Delta G^\circ_{1400K}$ = 1489.1 kJ / mol) [4]. The strong bond between zirconia and silica causes the mineral is very stable [5]. Nowadays, many methods of zirconia synthesis from zircon sand were developed. All of these methods generally have three main steps. First,

chemical or thermal decomposition of zircon. Second, selective dissolution in a solvent. Third, zirconium compound is separated from the rest of impurities [6].

Indonesia has an abundant reserve of mineral zircon, such as found in the Riau Islands, Borneo Island and Bangka Island. Zircon mineral will be a very bright prospect as a major source of zirconia-based ceramic material development if it can be processed in an appropriate manner. It is necessary a zirconia processing technique that can improve the quality of zirconia with a high purity level at the lowest possible cost.

Alkali fusion is a decomposition method that often used in the synthesis of zirconia. It is fusion zircon and alkali in a particular mole ratio at high temperature. Commonly, sodium hydroxide (NaOH) and sodium carbonate ($Na_2CO_3$) are often used in the synthesis of zirconia using alkali fusion method. However, the fact that the melting point of $Na_2CO_3$ was 2.5 times higher than that of NaOH (respectively 858.1 and 323 °C) favor the used of NaOH [7]. Another reason for using NaOH comes from its environmental effect compared with $Na_2CO_3$ which evolve $CO_2$ during the reaction with zircon.

Previously, Abdelkader et al. [4] reported that fusion zircon with equimolar mixture of KOH-NaOH requires a lower temperature compared to using of individual alkali. The reaction NaOH with zircon and KOH with zircon respectively can be represented by the following reaction:

$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O \quad (1)$$

$$ZrSiO_4 + 4KOH \rightarrow K_2ZrO_3 + K_2SiO_3 + 2H_2O \quad (2)$$

In this research, zirconia was synthesized from natural zircon sand that collected from Kereng Pangi, Central Kalimantan. NaOH, KOH and equimolar mixture of KOH-NaOH were used as alkali to decompose zircon in alkali fusion method. The phase composition and crystal structural study of the feed and the product was performed using X-ray diffraction (XRD).

## RESEARCH METHOD

For the zircon sand selected in this research, elements in the sand were qualitatively confirmed by X-ray Fluorescence (XRF) analysis. A flow chart of the process of $ZrO_2$ synthesis from the zircon sand by alkali fusion method is shown in Fig. 1. This research was started from the preparation of zircon sand collected from Kereng Pangi, Central Kalimantan. The zircon sand was separated from the magnetic particles by a magnet. After magnetic separation, it was crushed to 100 mesh and washed with water by an ultrasonic cleaner for 3 times.

Zircon sand which had been prepared was processed on the main step, the alkali fusion. In this step, zircon sand was mixed with alkali with a particular mole ratio and charged in stainless steel crucible. Alkalis used in this step are NaOH, KOH, and equimolar mixture of NaOH and KOH. The mole ratio between zircon sand and alkali for each fusion is 1: 4.8 (20% alkali excess from stoichiometric as theoretically determined from reaction (1) and (2)). Electric furnace was used to heat the mixture to the required fusion temperature at 700 °C for 3 hours.

Alkali fusion products was crushed using a mortar and then weighted before it leached with water to remove soluble compounds, such as sodium silicate, potassium silicate and any excess amount of alkali. Water leaching was performed three times using 300 ml of distilled water for 10 grams of alkali fusion product. Leaching was conducted by mixing the alkali fusion product and water into a beaker glass with a predetermined ratio, and then stirred using a magnetic stirrer with a speed of 200 rpm at room temperature for 1 hour for each step of leaching.

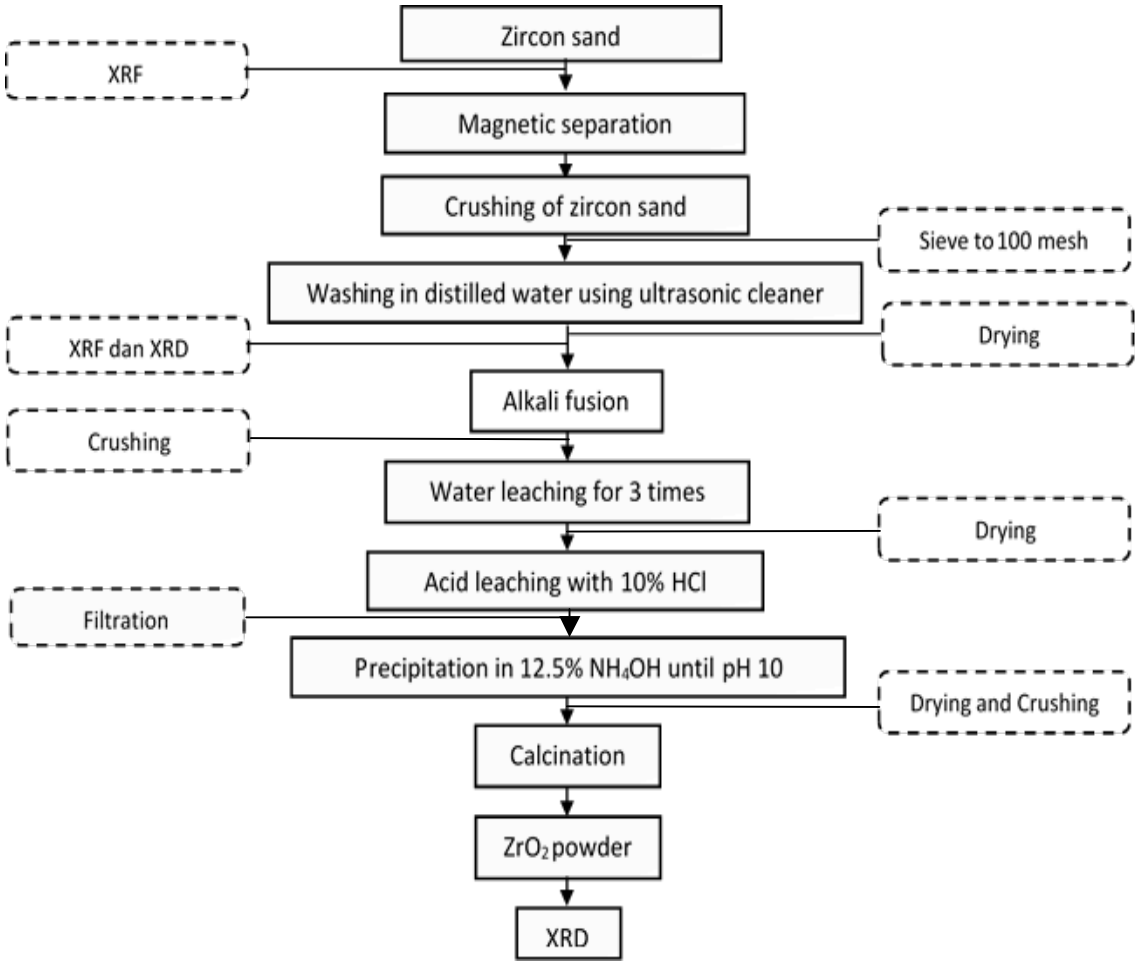


**Fig. 1.** Flow chart of the process of synthesis of $ZrO_2$ from the zircon sand by alkali fusion method

The solid hydrous zirconium obtained from water leaching was separated from the silicate solution and then dried. The dried powder was then leached with 300 ml of 10% HCl for 10 grams of dried powder to separate the acid soluble zirconium part from the unreacted zircon. The tools used in the HCl leaching same as the tools used in the water leaching. The HCl leaching was done with stirring speed of 200 rpm at room temperature for 1 hour, and its product was then filtered to obtain a yellow solution. The residue obtained is then dried and weighted. Percentage of zircon decomposition was then determined from the following equation:

$$\text{zircon decomposition (\%)} = \frac{\text{original weight of zircon-unreacted zircon}}{\text{original weight of zircon}} \times 100\ \%$$

HCl leaching product was precipitated in 10% ammonium hydroxide ($NH_4OH$) until the pH reached 10. The precipitate was filtered to separate the precipitate from $NH_4OH$ solution and dried in oven. It was then crushed and calcined at 500 °C for 3 hours in an electric furnace.

An X-ray diffractometer (XRD) X'Pert PRO (CuKα radiation, λ = 1.54060 Å) with a

step size 0.017° was used to obtain the XRD pattern for determination of crystalline phases and size of the zirconia powder. The refinement of the zirconia powder XRD patterns structural parameter was carried out by Rietica 1.7.7 program. Crystal size estimation of the zirconia powder was carried out by MAUD 2.33 program. Also, X-ray fluorescence (XRF) analysis was performed using a Philips E'xpert Pro to determine the composition of zircon sand.

## RESULT AND DISCUSSION

The XRD pattern of the zircon sand sample that has passed the preparation steps is shown in Fig. 2. The auto-matching indicates the presence of zircon, quartz, and rutile phase. X-ray fluorescence (XRF) analysis of it reveals that Zr (zirconium) with 90.9 wt.% is the major component of zircon sand, it has increased when compared to sample before preparation, which is 70.4 %. Other elements contained in the zircon sand sample are 2.99 wt.% Si, 3.59 wt.% Ti, 1.27 wt.% Hf and 0.27 wt.% Fe.

XRD is of great importance in the microstructure characterization of complex, multiphase and single phase materials. The application of XRD enables not only qualitative and quantitative phase analysis but also microstructure characterization (crystallite size, lattice distortions, dislocation densities, stacking faults and twins probability) [8]. The XRD pattern of sample fusion of zircon sand with NaOH (sample A) is shown in Fig. 3(a). It shows monoclinic $Na_2ZrO_3$ (PDF 00-035-0770) and orthorhombic $Na_2SiO_3$ (PDF 00- 082-0604) are the major phases of sample A. The XRD pattern of sample fusion of zircon sand with KOH (sample B) are shown in Fig. 3(b). It shows monoclinic $K_2ZrSiO_4$ (PDF 00-017-0282) is the major phase of sample B.

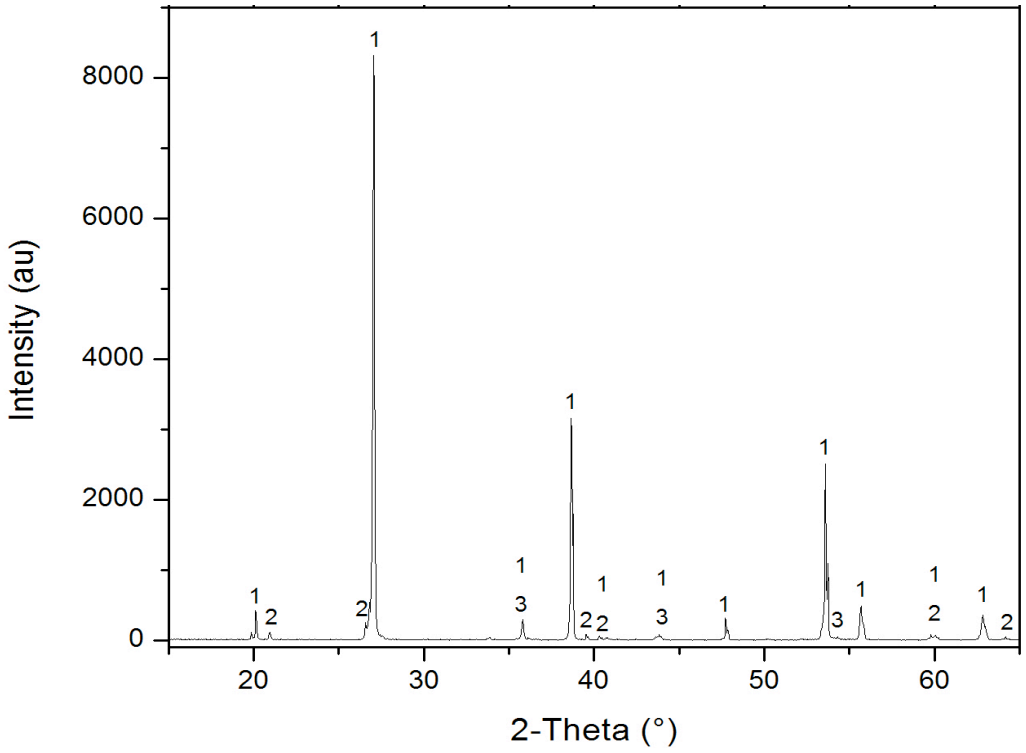


**Fig. 2.** The XRD pattern of the zircon sand sample: 1-zircon (PDF 00- 006-0266), 2-quartz (PDF 00-087-2096) and 3-rutile (PDF 00-076-1941). Figures in parentheses indicate the reference code numbers in the PDF-2 database.

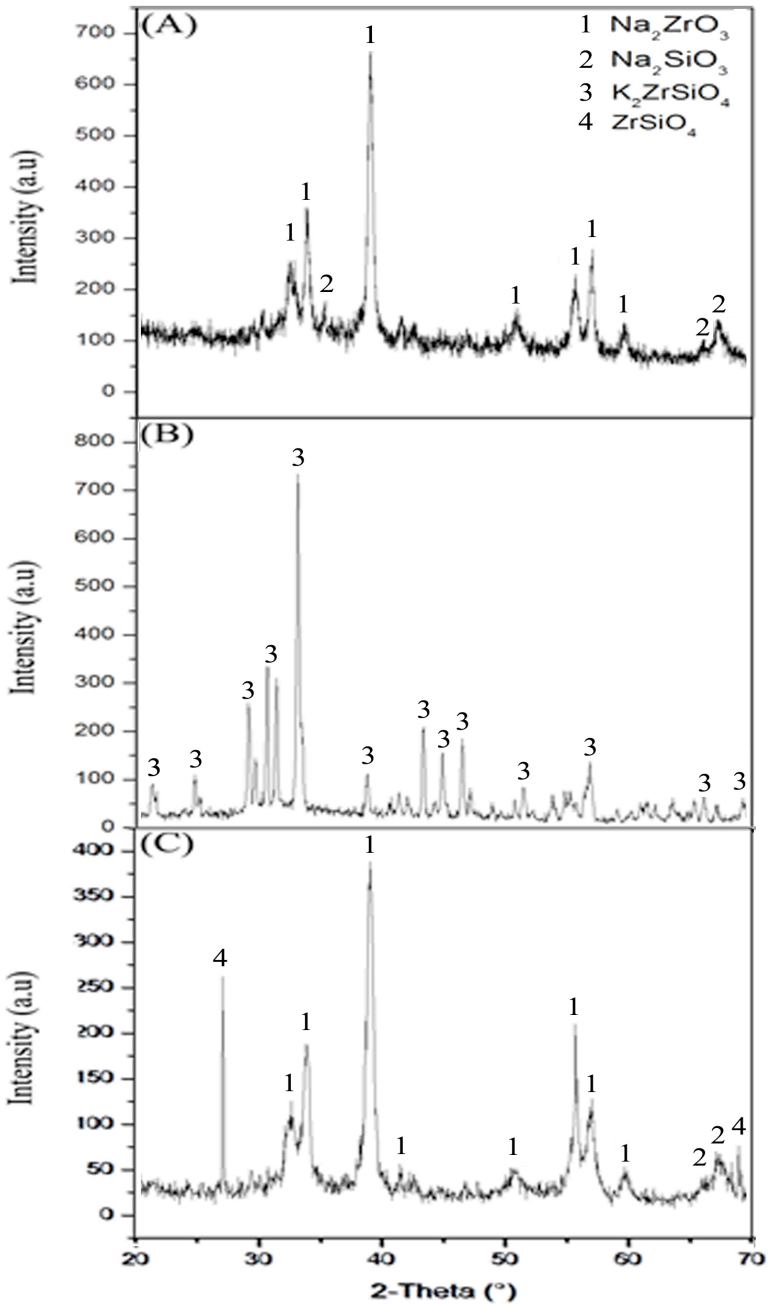


**Fig. 3.** The XRD patterns of sample fusion of zircon sand with (a) NaOH (sample A) (b) KOH (sample B) and (c) equimolar mixture of NaOH and KOH (sample C)

In sample A, the Zr and Si element will separate into different compounds during alkali fusion process, and then will dissociate during water leaching. In water leaching, $Na_2SiO_3$ will dissolve in water while $Na_2ZrO_3$ will precipitate. But in sample B, Zr and Si element are not separated into different compounds but is converted to the form of $K_2ZrSiO_4$ compound. In this case, Zr and Si element will dissociate during hydrochloric acid (HCl) leaching of the product. Therefore, the product produced in the sample B does not follow the reaction of (2), indicating that there is excess amount of KOH which does not react with zircon. This makes the sample B

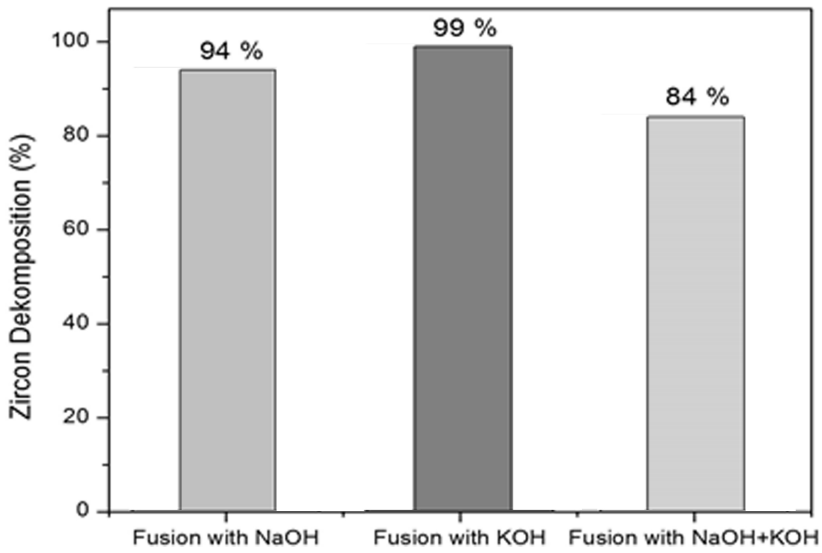


**Fig. 4.** Zircon decomposition

has a sticky and wet texture, it is because the excess KOH will react with $CO_2$ in the air and produce water. The excess of KOH will be separated in the water leaching process.

The XRD pattern of sample fusion of zircon sand with equimolar mixture of NaOH and KOH (sample C) is shown in Fig. 3(c). In sample C, mole ratio between zircon sand, NaOH and KOH respectively is 1: 2.4: 2.4, where the weight of NaOH and KOH is half of sample A and sample B. It shows monoclinic $Na_2ZrO_3$ (PDF 00-035-0770), orthorhombic $Na_2SiO_3$ (PDF 00-082-0604) and tetragonal $ZrSiO_4$ (PDF 00-006-0266). Equimolar mixture of NaOH and KOH is not effective in the decomposition of zircon, it can be seen in Fig. 3(c) that zircon peak is still visible on the XRD pattern. However, the decomposition in sample C is more effective by NaOH than KOH. It might be due to the melting point of NaOH lower than KOH. Decomposition by NaOH is earlier than KOH and then will be barrier to next decomposition of KOH. However, further research is needed to clarify and confirm the above explanation.

Fig. 4 shows the results of zircon decomposition. As shown in figure, sample A has the greatest percentage of zircon decomposition, which is 99%. However, the presence of water insoluble compound $K_2ZrSiO_4$ that will dissociate during the acid leaching increases the possibility of the silica content in the produced zirconium compounds. Sample C has the smallest percentage of zircon decomposition in accordance with the results of the XRD pattern analysis that still showed the presence of zircon peak.

The XRD patterns of zirconia powder were calcined at 500 °C for 3 hours are shown in Fig. 5. Analysis of the XRD pattern of sample A and sample B reveals the presence of single phase tetragonal zirconia ($ZrO_2$) (PDF 00-050-1089), whereas the XRD pattern of sample C reveals the amorphous zirconia. It indicates that the removal of water structure (dehydration process) from the amorphous hydroxide in sample C was not complete yet. The presence of the mound shape at small angles in the X-ray diffraction patterns of sample C suggest that the complete crystallization does not occur at these temperatures and the samples involve the cubic or tetragonal zirconia form and the $ZrO_2 \cdot nH_2O$ amorphous phase [9]. Therefore, it is unlikely that these patterns make it possible to identify reliably the cubic or tetragonal structure.

The results of refinement analysis of zirconia powder in sample A and sample B using Rietica program are shown in Table 1. The lattice parameters were obtained between the zirconia in sample A and sample B has a similar value, this indicates that there was no significant effect of NaOH and KOH during the alkali fusion to the zirconia lattice parameters were resulted. Table 2 shows the results of refinement analysis of zirconia powder in sample A

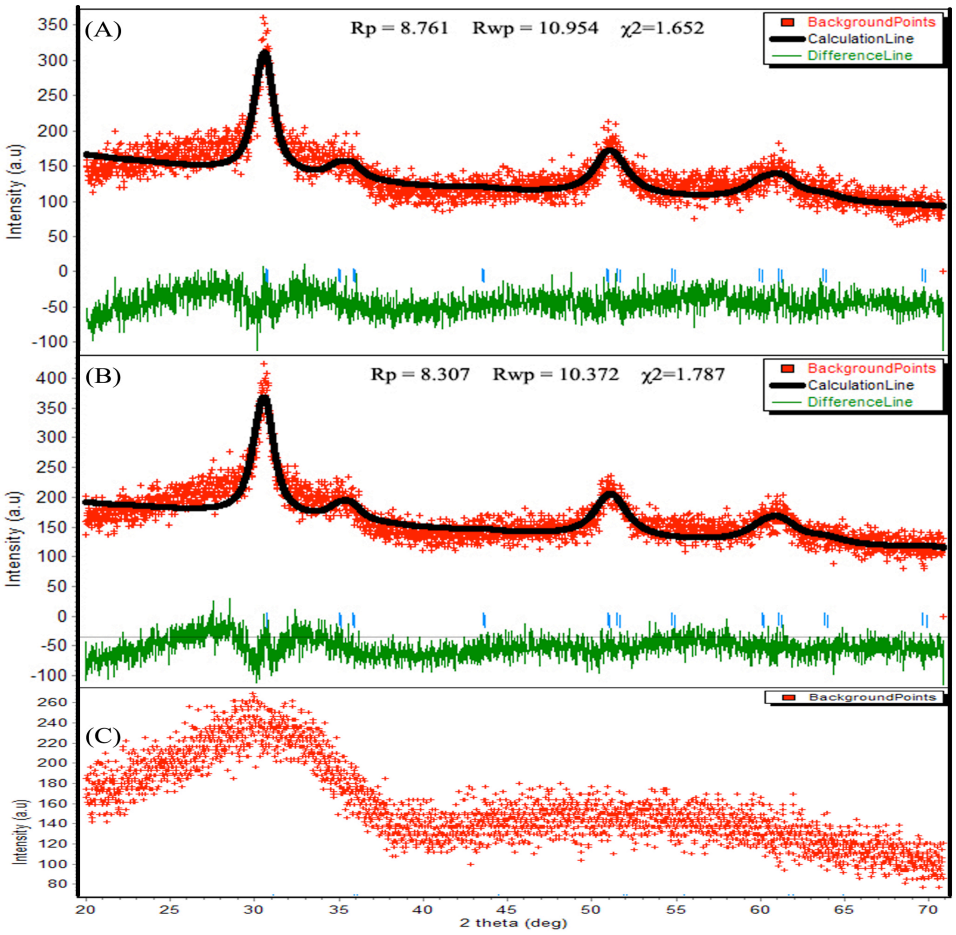


**Fig. 5.** XRD patterns of zirconia powder of (a) sample A, (b) sample B and (c) sample C were calcined at 500 °C for 3 hours.

and sample B using MAUD program. The peak width of XRD pattern is grain size and micro strain effect of material (after deducting by diffraction peak broadening of the effects of instrument) [10]. Analysis of crystal size estimation shows that the tetragonal zirconia can be categorized as nanocrystalline material, because it has crystal size estimation smaller than 100 nm. No significant difference was shown by the result of the crystal size estimation and micro strain between the zirconia in sample A and sample B, it actually can be seen qualitatively from similar peak width of both. Can be seen once again that there is no significant effect of the use of NaOH and KOH during the alkali fusion to the crystal size of zirconia were resulted.

**Table 1.** The results of refinement analysis of zirconia powder using Rietica program.

| Alkali | Phase (Space Group) | Lattice Parameter | | $V$ (Å$^3$) | $\rho$ (g/cm$^3$) |
|---|---|---|---|---|---|
| | | Rietveld | ICCD | | |
| NaOH | $ZrO_2$ ($P4_2/nmc$) | $a$=3,5465<br>$c$=5,1423 | $a$=3,5123<br>$c$=4,9888 | 64,6769 | 6,324 |
| KOH | $ZrO_2$ ($P4_2/nmc$) | $a$=3,5503<br>$c$=5,1286 | $a$=3,5123<br>$c$=4,9888 | 64,6421 | 6,328 |

**Table 2.** The results of refinement analysis of zirconia powder using MAUD program.

| Alkali | Phase (SG) | Crystal Size (nm) | Micro Strain ($\times 10^{-3}$) |
|---|---|---|---|
| NaOH | $ZrO_2$ ($P4_2/nmc$) | 50,2913 | 5,19594 |
| KOH | $ZrO_2$ ($P4_2/nmc$) | 49,7825 | 5,59386 |

## CONCLUSION AND SUGGESTION

The major conclusions and suggestions drawn from this research are as follows:

1. The major phases formed from the fusion of zircon sand and NaOH are monoclinic $Na_2ZrO_3$ and orthorhombic $Na_2SiO_3$; the fusion of zircon sand and KOH is monoclinic $K_2ZrSiO_4$; and the fusion of zircon sand and equimolar mixture of NaOH and KOH are monoclinic $Na_2ZrO_3$, orthorhombic $Na_2SiO_3$ and there is still unreacted zircon sand.
2. Fusion of zircon sand with 4.8 mol KOH has a greater zircon decomposition percentage than NaOH and equimolar mixture of NaOH and KOH, which is 99%.
3. Analysis of the XRD pattern of zirconia synthesized from fusion with NaOH and KOH were calcined at 500 °C for 3 hours reveals the presence of tetragonal phase, while the fusion with equimolar mixture of NaOH and KOH still shows amorphous.
4. Refinement analysis of zirconia synthesized from fusion with NaOH and KOH using Rietica and MAUD program shows that their lattice parameters and crystal size estimation has similar value, this indicates that there was no significant effect of the use of NaOH or KOH during the alkali fusion to the zirconia lattice parameters and crystal size estimation were resulted.

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