

## Double steps leaching and filtration in caustic fusion method to produce zirconia from local zircon concentrate

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### Abstract

A research on caustic fusion method of zircon concentrate has been conducted with applied single and double steps of leaching and filtration. The aims of research are to produce zirconia,  $\text{ZrO}_2$ , with high purity, to study its crystal structure and cell parameters and also comparing the results of single,  $\text{ZrO}_2(1)$ , and double steps,  $\text{ZrO}_2(2)$ . The results show that  $\text{ZrO}_2$  was successfully synthesized from high concentrate zircon, HG zircon. The  $\text{ZrO}_2$  was crystallized in tetragonal structure and space group of  $P42/NMC$ . The Fourier Plots of electron density of  $\text{ZrO}_2(1)$  and  $\text{ZrO}_2(2)$  at x, y and z axis show similar patterns. It indicates that the zirconia which was prepared by single and double steps leaching and filtration are the  $\text{ZrO}_2$  with similar structure. Few dissimilar on the electron density patterns are founded in x and z axis. It probably caused by the higher sodium oxide and silicon dioxide contents in  $\text{ZrO}_2(2)$ . as it were confirmed by X-Ray Fluorescence analysis. The existence of impurities may affect the electron density near ions in a unit crystal. This research found that double step leaching and filtration method does not enhance the efficiency on zirconia recovery it even allows high content of sodium and silicone ions in  $\text{ZrOCl}_2$  filtrate. The  $\text{ZrO}_2$  concentration in single step powder is 72.07 % and its 70.99 % in double steps powder.

**Keywords:** caustic fusion, leaching, zircon, zirconia, double leaching and filtration

### 1. Introduction

Zirconia receives much attention as ceramics and catalyst material due to its high thermal stability and its acidic/basic properties (Tanabe, 1996). Zirconia is also used as capacitors, metal oxide semiconductor, solid oxide fuel cells, highly reflective, and protective optical coatings (Bhattacharya and Tummala, 2000;

Rahmawati, et al., 2012). The use of zirconia in catalysis applications is promising because of high surface area (Bangsi et al., 2013). The zirconia based-electrode and electrolyte materials are still better choices until recently for solid oxide fuel cells, SOFC, due to good chemical stability at oxidized or reduced atmosphere, high electrical conductivity at proper temperature, geometrical stability in accordance with

their crystal structure eventhough under high operational temperature for long time operation.

Indonesia has not capable yet to produce the high quality zirconia and its still depend on the international distributors to fulfill the demands. Meanwhile, since 2010, some chemical industries and distributors have discontinued their zirconia product to be distributed in Indonesia. Therefore, it inhibites the progress on fuel cell researches and productions in the future. On the other hand, Indonesia actually has very potential abundant of zircon sand which is known as raw material for zirconia production. The abundants are spread over Kalimantan selatan, Riau islands, and Bangka-Belitung islands (Poernomo, 2012). Until at the beginning of 2000, zircon in Bangka Belitung islands was still treated as side product of Tin mining plant, that has low economic value. Then, some researchers, such as Soepriyanto and Hidayat (2006) could increased the zircon concentrate from side product of tin mining from less than 20% to became more than 98 % by applying modification on flowsheet separation method.

The zircon minerals are usually dissociated with 1 – 3 wt.% of hafnium (da Silva et al.,2012). A typical grade commercial zircon sand contains 65wt.% min.  $ZrO_2 + HfO_2$ , 32-33 wt.%  $SiO_2$ , 0.2 wt.%  $TiO_2$  and 0.15 wt.% max.  $Fe_2O_3$  (Sakom Minerals Co., Ltd., 2011 in da Silva 2012). The alkali fusion of zircon concentrates to produce zirconia is simple and requires only low capitals and operational cost. These makes alkali fusion as an important method on zirconium compounds production. However, only less informations in literature about practical view point, including the effect of some factors to the result of this alkali fusion method (da Silva et al., 2012).

This paper discuss the production of zirconia from High Grade zircon concentrate,that was procured from tin mining plant in Bangka Island. The method used was alkali or caustic fusion with modification on double leaching and filtration steps. The effectivity of method was analyzed base on the resulted powder in comparison with single step product. The parameter compared were crystallinity, crystal structure, electron density map, % recovery of  $ZrO_2$  and the contents of impurities.

## 2. Experiments

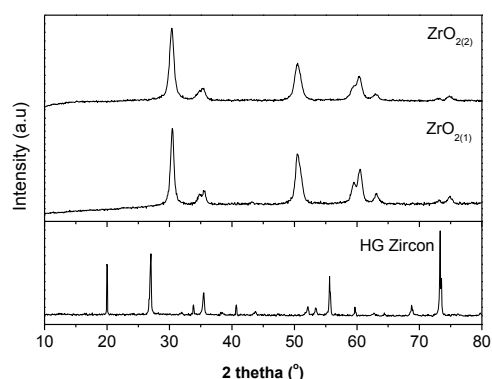
$ZrO_2$  was synthesized through caustic/alkali fusion method as conducted by Soepriyanto and Hidayat

(2006). In this research, the caustic method was modified by applying single and double steps leaching and filtration. Water leaching was conducted twice to get the second residu that has less sodium content. Acid, HCl solution, leaching also was conducted twice to recover more zirconium ion,  $Zr^{4+}$ , to react with chloride ions,  $Cl^-$  and producing  $ZrOCl_2$  solution. In this step, first and second filtrate were collected and then to be reacted with NaOH until the pH of solution reached 10 with continous stirring at 80 °C. After 24 hours aging, the sludge precipitated in the bottom of flask, was recovered by filtration and continued to be neutralized with hot water washing treatment. The recoverd sludge then to be heated at 150 °C for 3 hours and calcined at 800 °C for 5 hours to produce  $ZrO_2$  powder.

The prepared powder then were analyzed by XRD continued with Le Bail refinement to study its crsytallinity, the crystal structure, electron density mapping, and its cell parameters. Elemental and morphological analysis were also conducted by XRF and SEM, respectively. As a standard, the single step leaching and filtration were also conducted.

## 3. Results and Discussion

Zirconia powder was succesfully synthesized from High Grade Zircon,  $ZrSiO_4$ . The HG zircon was procured from Tin Mining plant, Bangka Island. The diffraction pattern of HG Zircon as raw material is depicted in Figure 1. Meanwhile, the diffraction pattern of powder produced by single step leaching and filtration, i.e  $ZrO_{2(1)}$  and the diffraction pattern of powder produced by double steps leaching and filtration, i.e  $ZrO_{2(2)}$  are described in Figure 1.



**Fig 1.** The diffraction patterns of HG Zircon,  $ZrO_{2(1)}$  and  $ZrO_{2(2)}$ .

The diffraction patterns shows that the products have different characteristic peaks in comparison to the characteristic peaks of HG Zircon as raw material. It indicates that the synthesise was conducted succesfully and it was confirmed by the peaks which are in agreement with diffraction pattern of  $ZrO_2$  standard of *Inorganic Crystal Standard Diffraction* (ICSD) # 66787 as it is described in Figure 2. The synthesized zirconia patterns show broad peaks that indicate lower crystallinity than ICSD #66787 standard.

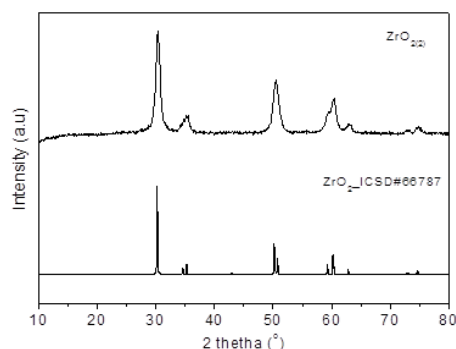


Fig. 2 Diffraction pattern of the prepared  $ZrO_2(2)$  in comparison to  $ZrO_2$  standard diffraction of ICSD # 66787

Le Bail refinement on XRD data of  $ZrO_2(1)$  and  $ZrO_2(2)$  also confirm the agreement between the patterns with standard ICSD # 66787. The Le Bail plots are described in Figure 3. Meanwhile the cell parameters are listed in Table 1.

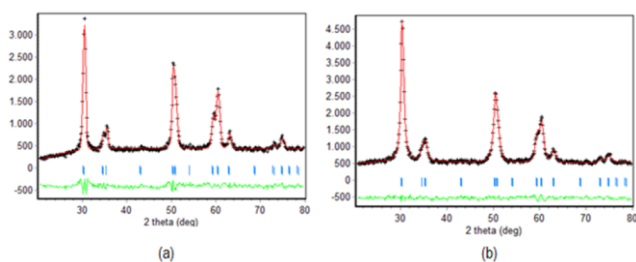


Fig.3 Le Bail plot of of (a)  $ZrO_2(1)$  and (b)  $ZrO_2(2)$

Table 1. Crystal structure and cell parameters of the prepared  $ZrO_2(1)$  and  $ZrO_2(2)$

| Cell parameters       | $ZrO_2(1)$     | $ZrO_2(2)$     |
|-----------------------|----------------|----------------|
|                       | Tetragonal     | Tetragonal     |
|                       | <i>P42/NMC</i> | <i>P42/NMC</i> |
| a (Å)                 | 3.592(1)       | 3.5855(5)      |
| b (Å)                 | 3.592(1)       | 3.5855(5)      |
| c (Å)                 | 5.192(2)       | 5.172(1)       |
| V (Å <sup>3</sup> )   | 67.00(4)       | 66.49(2)       |
| $\alpha=\beta=\gamma$ | 90             | 90             |
| Rp (%)                | 5.51           | 3.87           |
| Rwp (%)               | 6.75           | 3.52           |

The Fourier plots of the electron density of  $ZrO_2(1)$  and  $ZrO_2(2)$  at x, y and z axes are depicted in Figure 4, 5 and 6, respectively. The plots show that the electron density around ions in  $ZrO_2(1)$  and  $ZrO_2(2)$  at 3 axes are identical. However, a few different on patterns actually present at 3 axes. The presence of impurities may affect the electron distribution, and it found that the kind of impurity content inside both powder are similar, however the quantities are different.

Those impurities were also found by Liu et al. (2014) who produced Zirconia from Brazilllian zircon. The sodium silicate that formed during mixing process with NaOH is dissolved during water leaching and hydrolyzed into  $H_2SiO_3$ . Meanwhile, sodium zirconate,  $NaZrO_3$  is hydrolyzed into  $ZrO(OH)_2$ . At caustic fusion process,  $Na_2ZrSiO_5$  is also formed from reaction between NaOH and  $ZrSiO_4$ . The  $Na_2ZrSiO_5$  then reacted with HCl during acid leaching producing  $ZrO(OH)_2 \cdot SiO_2$  and  $NaCl \cdot ZrO(OH)_2$ . As the final result, the composition found by Liu et al. (2014) was  $ZrO_2$ ,  $SiO_2$  and  $Na_2O$  at 57.169%, 6.77 % and 7.049 %, respectively.

XRF analysis confirmed the quantity and kind of impurities contained in the prepared  $ZrO_2$ . The result is listed in Table 2. XRF analysis shows that caustic fusion method remains sodium oxide,  $Na_2O$ , at 14.71 % of content in  $ZrO_2(1)$  and 14.91 % of content in  $ZrO_2(2)$ .

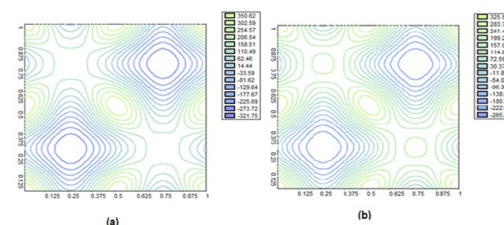


Fig. 4 The Fourier plot of electron density around anion and cations at Z axe ( slice 1) in (a)  $ZrO_2(1)$  and (b)  $ZrO_2(2)$ .

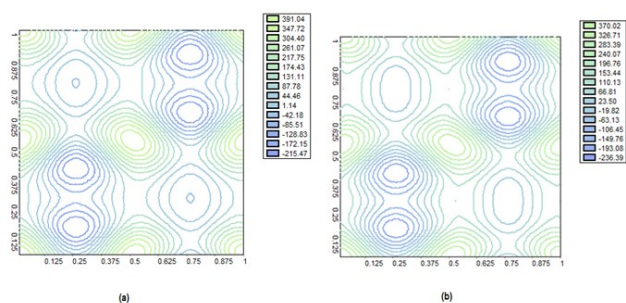


Fig. 5 The Fourier plot of electron density around anion and cations at X axe ( slice 1) in (a)  $ZrO_{2(1)}$  and (b)  $ZrO_{2(2)}$ .

Table 2. The elemental analysis results on HG Zircon and the prepared materials.

| Impurities | Content in materials (%) |              |              |        |
|------------|--------------------------|--------------|--------------|--------|
|            | HG Zircon                | $ZrO_{2(1)}$ | $ZrO_{2(2)}$ | Residu |
| $ZrO_2$    | 64.10                    | 72.07        | 70.99        | 57.95  |
| $SiO_2$    | 14.67                    | 3.03         | 3.60         | 7.09   |
| $Na_2O$    | 11.61                    | 14.71        | 14.91        | 19.89  |
| $Al_2O_3$  | 1.33                     | 0.94         | 0.96         | 1.66   |
| $SO_3$     | 1.85                     | 0.93         | 0.91         | 1.39   |
| $MgO$      | -                        | 2.56         | 2.65         | 3.33   |

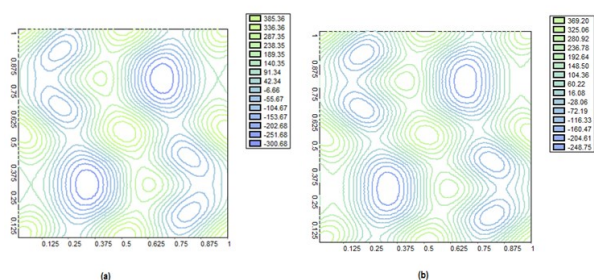


Fig. 6 The Fourier plot of electron density around anion and cations at Y axe ( slice 1) in (a)  $ZrO_{2(1)}$  and (b)  $ZrO_{2(2)}$ .

#### 4. Conclusions

$ZrO_2$  has been synthesized successfully from HG zircon as side product of tin mining plant, Bangka Island. The  $ZrO_2$  was crystallized in tetragonal structure and space group of  $P42_1NMC$ . The prepared powder produced by double and single leaching and filtration method have similar structure and identical electron density map at x-y-z axis. A few dissimilar is confirming by the presence of impurities at different content. The content of sodium oxide and silicon oxide are higher in powder produced from double steps leaching and filtration. It indicates that the double

treatment does not provide any advantages in zirconia manufacturing.

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#### References

1. F. Rahmawati, B. Prijamboedi, S. Soepriyanto, Ismunandar, SOFC composite electrolyte based on LSGM-8282 and zirconia or doped zirconia from zircon concentrate, *Int. J. Min. Met. Mat.* **19**(9)(2012)863-871.
2. H. Poernomo, Informasi umum zirkonium (in Indonesian) General Information on zirconium, Badan Tenaga Nuklir Nasional, Pusat Teknologi Akselerator dan Proses Bahan, Yogyakarta (2012)
3. K. Tanabe, Surface and Catalytic properties of  $ZrO_2$ , *Material Chemistry and Physics*. **13** (1996) 347-364.
4. R. Liu, J. Qu, J. Song, T. Qi, A. Du, Analysis of water leaching and transition processes in zirconium oxychloride octahydrate production, *Ceramics International*. **40** (2014) 1431-1438.
5. R.J. da Silva, A.J.B. Dutra, J.C. Afonso, Alkali fusion followed by a two-step leaching of a Brazilian zircon concentrate, *Hydrometallurgy*. **117-118**(2012) 93-100.
6. S.K. Bhattacharya, R.R. Tummala, Next generation integral passives: materials, process, and integration of resistor and capacitors on PWB substrates, *J. Mat. Sci: Materials in Electronics II*(2000)253-268.
7. S. Soepriyanto, T. Hidayat, Synthesis of nanocrystalline zirconia from by product of tin processing, in *Proc. Int. Conf. Mathematics and Natural Sciences (ICMNS)* (Bandung, Indonesia, 2006).
8. U.K.H. Bangi, C. Sun-Park, S. Baek, H. Ho-Park, Sol-gel synthesis of high surface area nanostructured zirconia powder by surface chemical modification, *Powder Tech.* **239** (2013) 314-318.