

Structure and morphological analysis of various composition of yttrium doped-zirconia prepared from local zircon sand

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Abstract. Yttrium ions, Y^{3+} were doped into ZrO_2 that was synthesized from zircon sand. Zircon sand is a side product of tin mining plant in Bangka Island, Indonesia. Solid state reaction was chosen as the method to dope yttrium ions from Y_2O_3 into ZrO_2 at various % mol of 4.5; 8 and 10. This research aims to understand the crystal structure, morphological analysis and particle size analysis. The X-ray diffraction analysis equipped with Le Bail refinement found that the prepared ZrO_2 is in two phases of the monoclinic and tetragonal structure, and the structure changed to cubic after yttrium ions doping. However, the monoclinic and tetragonal still exist. Various yttrium concentrations provide different morphology, in which 4.5 YSZ shows a blocking phase indicated as the presence of impurities. The blocking phase seems to prevent sintering and allows a line crack on the material layer. Meanwhile, 8YSZ and 10YSZ show homogeneous morphology and without provides a line crack. The mean particle size after sintering is in between 1.1 – 1.5 μm .

1. Introduction

Indonesia has tin ore abundant spread over Pulau Karimun, Singkep, in some of the Sumatera lands, and also in Bangka Island, Riau islands, until to the west Kalimantan [1]. Among of those, Bangka island has the largest Tin abundant with a side product is zircon sand ($ZrSiO_4$). Zircon, $ZrSiO_4$, is a stabil molecule due to the strong bond between zirconia and silica. Some methods to extract zirconium from zircon are caustic fusion or with soda ash [2], heat plasma dissociation [3]. Zirconia, ZrO_2 , is an oxygen ions conductor with high flexibility and high resistance [4]. It is used as a material for the oxygen sensor, fuel cell material, thermal barrier coating, and some high temperature applications. Tetragonal zirconia has high mechanical strength, meanwhile cubic zirconia has high ionic conductivity [5]. The addition of some metal oxides such as MnO , NiO , Cr_2O_3 , Fe_2O_3 , Y_2O_3 and Ce_2O_3 could stabilize tetragonally and cubic phase of zirconia at room temperature [6].

A high ionic conductivity of material is required to develop a solid oxide fuel cell, SOFC. Cubic zirconia is known to have highest ionic conductivity. However, the structure is not stable at room temperature. Doping of yttrium ions into zirconia is known to stabilize the cubic structure at room temperature and increase the ionic conductivity due to the formation of oxygen vacancies when Zr^{4+} is replaced by Y^{3+} [7]. Low yttrium concentration might produce tetragonal zirconia that has good mechanical strength, meanwhile high concentration of yttrium dopant might produce cubic structure zirconia that has high ionic conductivity [5]. In this research the zircon sand from Bangka island was used as raw material for zirconia production. Then the prepared zirconia, ZrO_2 , was doped with yttrium ions, producing yttria stabilized-zirconia, YSZ, to enhance their electrical conductivity. The yttrium doping was conducted by solid state reaction method, as the most simple method to prepare some inorganic materials [8]. Analysis of structure and electrical conductivity were conducted to



identify the prepared materials at various yttrium ion concentration and to know their functional properties in comparison with the commercial YSZ.

2. Experiment

Zirconia, ZrO_2 was synthesized with caustic fusion method [9] in which the zircon sand concentrate, ZrSiO_4 , was crushed with NaOH at a ratio of ZrSiO_4 : NaOH 1:4. The mixture was then heated at 800 °C to produce a greyish white powder. The powder then was leached with distilled water at a volume ratio of 1:10 of powder to water, and followed by filtration. Next step was to leach residue of filtration with 3.5 M of HCl at a volume ratio of 1:10, means that 1 gram of residue was dissolved in 10 mL HCl, at 80 °C and under stirred condition. The result was a cloudy yellow solution that produced a clear yellow solution after filtration. The yellow solution is $\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$ (ZOC). Zirconia, ZrO_2 , was precipitated from ZOC by slowly added 3 M of NH_4OH . A white precipitate was produced. After decantation and heating at 800 °C for 5 hours, a white powder of ZrO_2 was founded.

A mixture of Y_2O_3 and ZrO_2 was crushed for 2 hours in a pestle at a stoichiometric ratio to produce a 4.5 %, 8 % and 10 % mol of yttrium. Calcination was at 1000 °C for 2 hours, then followed by sintering of its green pellets at 1500 °C for 5 hours. X-ray diffraction analysis equipped with Le Bail refinement was used to identify the peaks in comparing with YSZ standard diffraction, and also to analyse its crystallinity, crystal structure, and its cell parameters. The prepared materials also were analyzed by SEM to understand their surface morphology and were analyzed with LCR meter (GW Instek) to study their impedance plot and their electrical conductivity. The impedance was measured at 20 Hz – 5 MHz at 300 – 700 °C.

3. Result and Discussion

Synthesis of zirconia from ZrSiO_4 occurs in some steps to produce Na_2ZrO_3 , ZOC, $\text{Zr}(\text{OH})_4$ and then ZrO_2 . The reactions can be read in our previous publication [9]. The diffraction pattern of the prepared ZrO_2 in comparison with standard diffraction of tetragonal and monoclinic ZrO_2 is depicted in Figure 1. Compare to the standard diffraction, the diffraction peaks are broader indicating lower crystallinity. The specific peaks of ZrO_2 are identified at 20~30.30 °; 34.70 °; 35.24 °; 50.34 ° and 60.26 °. Meanwhile a peak at 20~28.36 ° confirms the present of monoclinic phase ZrO_2 based on ICSD#157403.

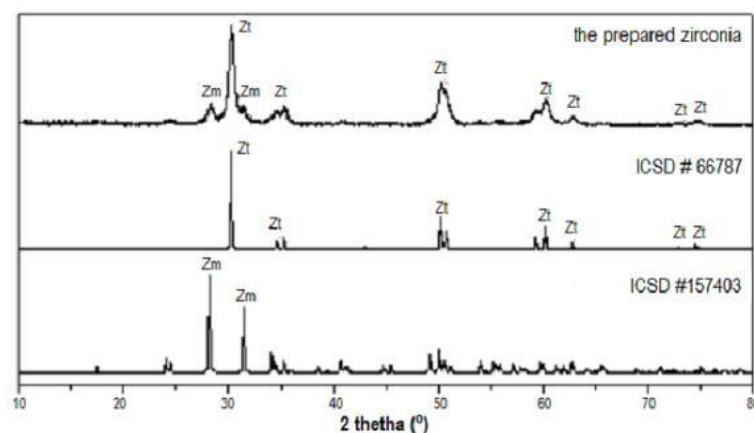
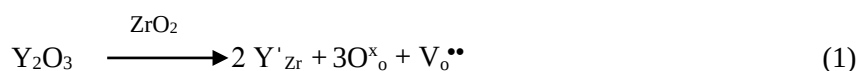


Figure 1. Diffraction pattern of the prepared zirconia compared to the standard diffraction of tetragonal zirconia, ICSD #66787 and monoclinic zirconia, ICSD#157403

A Le Bail refinement that was applied by RIETICA software confirmed the presence of those two phases of tetragonal (space group of $P4_2/NMc2$) and monoclinic (space group of $P121/C1$) with cell parameters as listed in Table 1. This result is in agreement with our previous result [9] and it confirms the reproducibility of the synthesis method. Doping of yttrium ions into zirconia was conducted by solid state reaction to produce YSZ at various % mol of yttrium. Two moles of Y^{3+} replaced Zr^{4+} at its crystal site to produce 1 mole vacancy, $\text{V}_\text{O}^{\bullet\bullet}$, to compensate the lack of positive charge. The stoichiometrical reaction is described in Kroger-Vink Notation (equation (1)).

Tabel 1. The Le Bail refinement result of the diffraction data of the prepared ZrO₂

Cell parameters	Zirconia	
	phase 1 (ZrO ₂ m)	phase 2 (ZrO ₂ t)
	ICSD#157403	ICSD#66787
	Monoklinik	Tetragonal
	<i>P</i> 1 21/ <i>C</i> 1	<i>P</i> 42/ <i>N</i> <i>M</i> <i>C</i> <i>z</i>
a (Å)	5.233428	3.598713
b (Å)	5.039176	3.598713
c (Å)	5.727037	5.1931
V (Å ³)	150.172928	37
α=β=γ	α=γ=90; β=96.12	67.254959
Rp (%)		90
Rwp (%)		6.12
		6.93



The diffraction patterns of YSZ at the various composition of yttria are depicted in Figure 2.

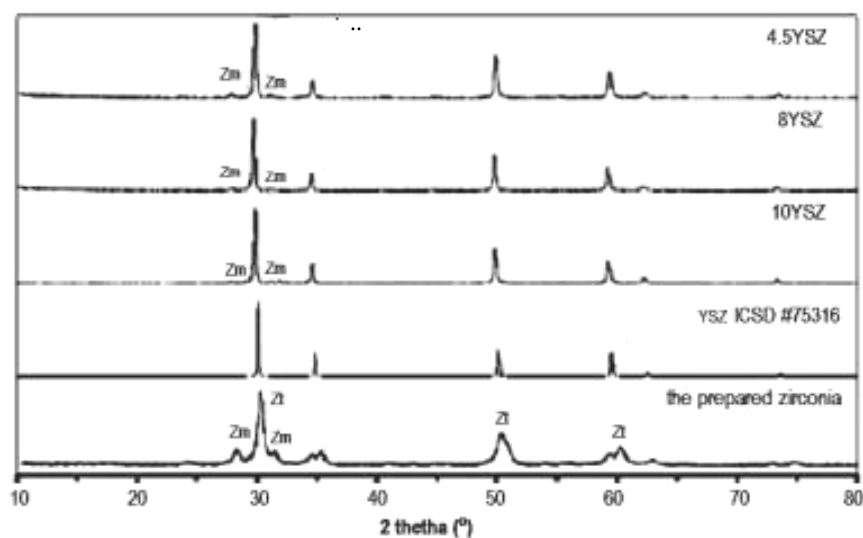


Figure 2. The diffraction patterns of YSZ at various composition.

Figure 2 shows that the materials have specific peaks as YSZ ICSD#75316 at 20~30,8°; 34,92°; 50,15°; dan 59,52°. Meanwhile, small peaks at 20~27,91° dan 31,09° confirm the presence of monoclinic phases. It indicates that the yttrium doping did not eliminate the presence of monoclinic zirconia in the prepared zirconia from zircon sand. Le Bail refinement confirms that the materials are in cubic phase with the existence of tetragonal and monoclinic phases. The refinement result is listed in Table 2,3, and 4. Meanwhile, the Le Bail plots are depicted in Figure 3. The refinement shows that yttrium doping into ZrO₂ allows cell parameter to decrease from 3.598713 (Å) into 5.135102 (Å), 5.162044 (Å), and 5.153061(Å) for 4.5YSZ, 8YSZ, and 10YSZ, respectively. It indicates the replacement of Zr⁴⁺ by Y³⁺, in which the atomic size is smaller than Zr⁴⁺.

Table 2. Cell parameters of 4.5 YSZ as resulted from Le Bail refinement by applying monoclinic, tetragonal and cubic phases.

Cell parameters	phase 1 (ZrO ₂ m)	phase 2 (ZrO ₂ t)	Phase 3 (4,5YSZ)
	ICSD#157403	ICSD#66787	ICSD#75316
	Monoclinic	Tetragonal	cubic
	<i>P 1 21/C 1</i>	<i>P 42/N M C z</i>	<i>F M 3 M</i>
a (Å)	5.137639	3.631561	5.135102
b (Å)	5.223372	3.631561	5.135102
c (Å)	5.345530	5.164413	5.135102
V (Å ³)	141.690506	68.109474	135.408920
$\alpha=\beta=\gamma$	$\beta=98.987$; $\alpha=\gamma=90$	90	90
Rp (%)		6.92	
Rwp (%)		7.47	

Table 3. Cell parameters of 8YSZ as resulted from Le Bail refinement by applying monoclinic, tetragonal and cubic phases.

Cell parameters	phase 1 (ZrO ₂ m)	phase 2 (ZrO ₂ t)	phase 3 (8YSZ)
	ICSD#157403	ICSD#66787	ICSD#75316
	Monoclinic	Tetragonal	cubic
	<i>P 1 21/C 1</i>	<i>P 42/N M C z</i>	<i>F M 3 M</i>
a (Å)	5.177034	3.643075	5.162044
b (Å)	5.218873	3.643075	5.162044
c (Å)	5.309533	5.166026	5.162044
V (Å ³)	141.691360	68.563469	137.551392
$\alpha=\beta=\gamma$	$\beta=98.99$; $\alpha=\gamma=90$	90	90
Rp (%)		9.87	
Rwp (%)		14.93	

Table 4. Cell parameters of 10YS as resulted by Le Bail refinement by applying monoclinic, tetragonal and cubic phases.

Cell parameters	phase 1 (ZrO ₂ m)	phase 2 (ZrO ₂ t)	phase 3 (10YSZ)
	ICSD#157403	ICSD#66787	ICSD#75316
	Monoclinic	Tetragonal	cubic
	<i>P 1 21/C 1</i>	<i>P 42/N M C z</i>	<i>F M 3 M</i>
a (Å)	5.157311	3.598692	5.153061
b (Å)	5.213131	3.598692	5.153061
c (Å)	5.349006	5.168529	5.153061
V (Å ³)	142.194382	66.935455	136.834610
$\alpha=\beta=\gamma$	$\beta=98.60$; $\alpha=\gamma=90$	90	90
Rp (%)		9.63	
Rwp (%)		15.32	

SEM analysis (Figure 4) on the prepared materials shows a different morphology between that various composition. A Software, MeasureIT (a free edition) that was used to analyse the SEM images found that particle size of 4.5YSZ is $1.58 \pm 0.544 \mu\text{m}$. Meanwhile, the particle size of 8YSZ and 10YSZ are $2.021 \pm 0.716 \mu\text{m}$ and $1.529 \pm 0.498 \mu\text{m}$, respectively. A histogram was developed to understand the highest probability particle size, and it was in between $1.1 - 1.5 \mu\text{m}$.

Figure 4(a) shows a heterogeneous surface morphology with the presence of blocking phases, as shown by a white circle in Figure 4(a) and clearly shown in Figure 5. Those blocking phase may indicate the presence of silica rich surface, as it also found by our previous research [10] in the preparation of doped- ZrO_2 and composite of ZrO_2 -LSGM8282 in which the blocking phase presented when the ZrO_2 used was prepared from Indonesian local zircon.

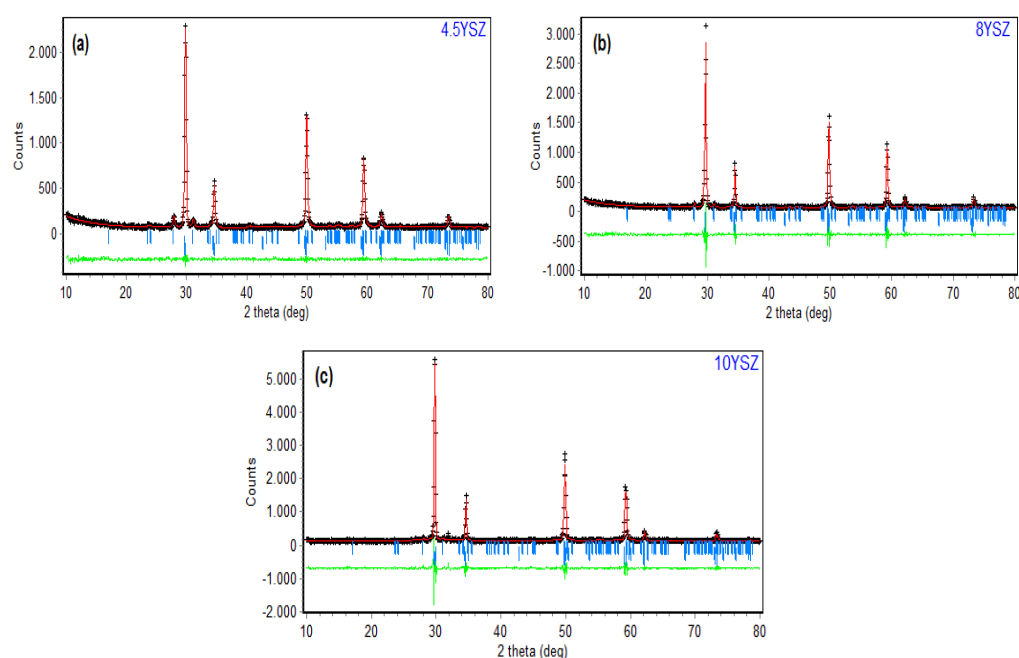


Figure 3. The Le Bail plots of 4.5YSZ(a), 8YSZ(b), dan 10YSZ(c) as resulted from refinement by applying 3 phases of tetragonal, monoclinic and cubic. + is the experimental data, there line is calculation line, and the green line is different between data and calculation.

Those blocking phase was not found in the composite prepared from commercial ZrO_2 . The XRF analysis of ZrO_2 that was synthesized from local zircon found the presence of 3.03 % of silica and 14.71 % of sodium oxide. The sodium oxide content might come from NaOH used as destruction agent. It would release during the sintering process at 1500°C for 5 hours. Liu et al.[11] also found such impurities when producing zirconia from Brazilian zircon. The sodium silicate is formed during mixing process between zircon sand and NaOH, and it hydrolized into H_2SiO_3 during water leaching. Caustic fusion process also results in $\text{Na}_2\text{ZrSiO}_5$ which then reacts with HCl during acid leaching to produce $\text{ZrO}(\text{OH})_2\text{-SiO}_2$ and $\text{NaCl.ZrO}(\text{OH})_2$. As the final result the composition of ZrO_2 , SiO_2 , and Na_2O were 57.169%, 6.77% and 7.049% , respectively[11]. The presence of blocking phase seems to prevent sintering process then it causes line crack as described by Figure 4(a2). Meanwhile, at a high content of yttrium ions of 8YSZ and 10YSZ the blocking phase and a line crack did not exist. It seems that the high content of yttrium ions prevent the impurities to leach out to the surface and inhibit the sintering process. A detailed study is required to understand the mechanism of those such preventing process and to study the material in term of their chemical composition at before and after sintering process, and the detail effect on grain and grain boundary ionic conduction.

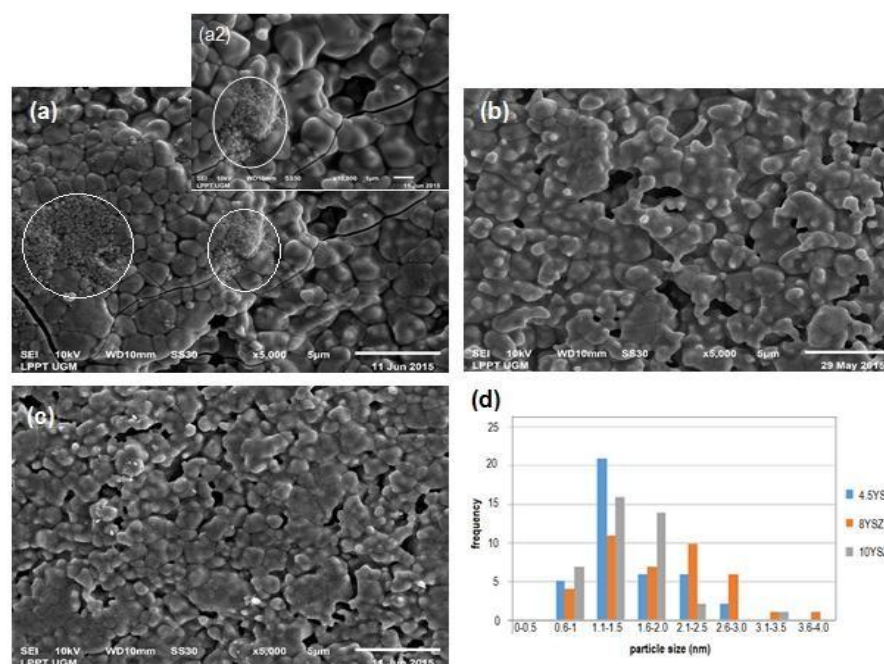


Figure 4. SEM images of 4.5YSZ(a) and 4.5YSZ at high magnification(a2) that showing a blocking phase and line crack, 8YSZ(b), and 10YSZ (c), and the hystogram of particle size distribution (d)

4. Conclusion

Yttrium stabilized zirconia that was prepared from local zircon sand consist of three phases, i.e cubic, monoclinic and tetragonal structure. A high content of yttrium, i.e 8YSZ and 10YSZ show a homogeneous morphology. Meanwhile, the 4.5YSZ shows a blocking phase indicating the presence of silica rich phase. This blocking phase seems to prevent the sintering process that leads to forming a line crack on the material layer. The particle size is ranging from 1.1 – 1.5 μm .

5. References

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