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Zirconium Oxide X-ray Diffraction Data Processing ByRietveld Analysis Method

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ABSTRACT

X-ray Diffraction experiment was carried out on zirconium oxide synthesized from zircon sand ($ZrSiO_4$), originally extracted from mines located in the Indonesian Island of Borneo. Zirconium hydroxide ($Zr(OH)_4$) was extracted from $ZrSiO_4$ after filtering the sample by a hydro-metallurgy process. Zirconium hydroxide was calcinated to obtain zirconium oxide due to decomposition of hydrogen compound. The diffraction experiment on zirconium oxide was carried out in the 2θ scattering angle range of 20^o - 100^o. JCPDS data asserts that the zirconium oxide sample contains three distinct phases, ZrO, Zr_2O and ZrO_2. Results of the Rietveld analysis refinement procedure seems to agree with the three-phase model assumption. The result shows that the fractional composition of the zirconium oxide is 0.69% ZrO, 40.2% Zr_2O, and 59.12% ZrO_2 with structure models of face centered cubic, primitive cubic and orthorhombic respectively. Fourier analysis electron density map of the (001) plane shows the absence of covalent bonds between Zr-O atoms and that the electrons are asymmetrically distributed around the atoms with a strong vibrational direction in the tetrahedral direction.
KEYWORDS: zircon, zirconium oxide, Rietveld analysis methode, calcination.

INTRODUCTION

Recent research on materials has developed into an interdisciplinary field in materials science. An important area in materials science research is the synthesis and processing of materials from a variety of natural starting materials, such as minerals extracted from existing mines. Zircon Oxides are synthesizedfrom zircon sand as raw minerals. Concentrate zircon sand obtained from Indonesian mines; most of the proven reserves of these raw minerals are found in the Central and West Kalimantan provinces[1].Specific reference on the synthesis of the zirconium oxides could be found in another paper [2].

X-ray diffraction techniques provide one of the non-destructive methods of phase analysis as well as mapping of the electronic density in materials. The purpose of this investigation is to identify the refined X-ray diffraction intensity profile and to determine the fractional quantity of various zirconium oxides phases in the $ZrSiO_4$powder which has been specially prepared in the laboratory in order to obtain a mixture of zirconium oxides phases, ZrO, Zr_2O, and ZrO_2respectively [1,2]. Results of structural analysis of Zirconium Oxides using the Rietveld refinement method and maps of the electron density of the major phases obtained from Fourier analysis method using *Fullprof* application code are then presented and discussed.

METHODS

Sample Preparation

The starting raw material is the zircon sand ($ZrSiO_4$) extracted from mines in central- and west Kalimantan province;The natural zirconsandfractional compositionisshowninTable-1, and the natural physical appearance of the zircon sands is shown in Figure2 [1,2].

Table-1.Zircon sand chemical composition

substance	ZrO_2	SiO_2	Fe_2O_3	TiO_2
composition (%)	66.21	27.82	3.6	1.4

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Figure 1.100 mesh zirconium sand ($ZrSiO_4$), with the reddish chocolate colour.
The copper-coloured coin is shown for colour comparison.

Zirconium Oxides are obtained as an extraction product from $ZrSiO_4$by a hidro-metallurgymethod. In this procedure, sodium hydroxide Na(OH) is used as the reagent materials for fusion reaction; sulfate acid (98% H_2SO_4) is used for leaching agent and purification.

The first step is to decompose the zircon sand ($ZrSiO_4$). The zircon sand was mixed with sodium hydroxide (NaOH) and was stirred until a homogenous mixture is obtained, followed by pouring the mixture into a stainless steel container (316L type), and then heating itat 700^{o}C for one hour. At that temperature the zircon sand would be decomposing into sodium zircon silicate($NaZrSiO_5$) and sodium silicate ($NaSiO_3$). The reaction equation is

$$2ZrSiO_4 + 6NaOH \rightarrow Na_2ZrO_3 + Na_2ZrSiO_5 + Na_2SiO_3 + 3H_2O$$

In the next step, the hydrolysis method is used to obtain deposits of zircon hydroxide from Na_2ZrSiO_5. Purification of thedeposite zircon hydroxide $Zr(OH)_4$was used H_2SO_4 leaching, its reaction is

$$Zr(OH)_4 + 2H_2SO_4 \rightarrow Zr(SO_4)_2 + 4H_2O$$

Obtaining pure $Zr(OH)_4$deposite was carriedout by setting pH = 7 of $Zr(SO)_4$ solution. $Zr(OH)_4$ powder obtained of filtering $Zr(OH)_4$ deposits. Finally, the zirconium oxide (ZrO_2) was obtained by calcinating zirconium hydroxide($Zr(OH)_4$) at900^{o}C.

Structure characterization

Zircon Oxides powder sample has been pelletized by using a press machine and a dies having a 15 mm diameter and a thickness of around 10 mm. Powderstep-scan X-ray diffraction measurements were performed on the zircon oxides pellet using a Rigaku X-ray diffractometer (Cu Kα radiation, λ= 1.5405 Å)at the Islamic State University (UIN) laboratory with a step of 0.02° in the 2θ angular range from 20° - 100°.The refinement of the zircon oxides powder X-ray patterns structural parameters was carried out by RIETAN (Rietveld Analysis) analysis code developed by F. Izumi [5,6].For the RIETAN iteration process, a pseudo-Voigt profile function and modified Marquardt iteration methods are used [7,8]. The refined parameters consist of the global parameters; these are the background- and shift parameters, and the phase-dependent parameters such as the lattice parameters, isotropic thermal factor and anisotropic, preferred orientation parameter atomic occupation factor, and also atomic position in the unit cell. Using suitable crystallographic information available in the JCPDS- International Center for Diffraction Data and by qualitative comparison with the measured XRD intensity, three distinct phases ZrO, Zr_2O and ZrO_2could be identified in the sample and used as initial input parameters in the refinement process of zirconium oxide.

RESULTS AND DISCUSSION

Rietveld analysis

The input parameters used in the Rietveld analysis are the space group models of the three compounds above, which are the cubic Fm3m and Pn3m with the tetragonal P-4m2(international short symbol) respectively [3,4], and other initialized structural and profile parameters. The space group and the crystal system inputs are shown in Table-2:

Table-2. Space group and the crystal system input

No	Compounds	Space group	Crystal system & Laue symmetry class	preferred orien-tation vector	anisotropic axis
1	ZrO	Fm3m	Cubic, m3m	(1,0,0)	(0,0,1)
2	Zr_2O	Pn3m	Cubic, m3m	(1,0,0)	(0,0,1)
3	ZrO_2	P-4m2	Tetragonal, 4/mmm	(1,0,0)	(0,0,1)

Both theexperimental X-ray diffractionpattern and the RIETAN refinement resultsare showninFigure 2.

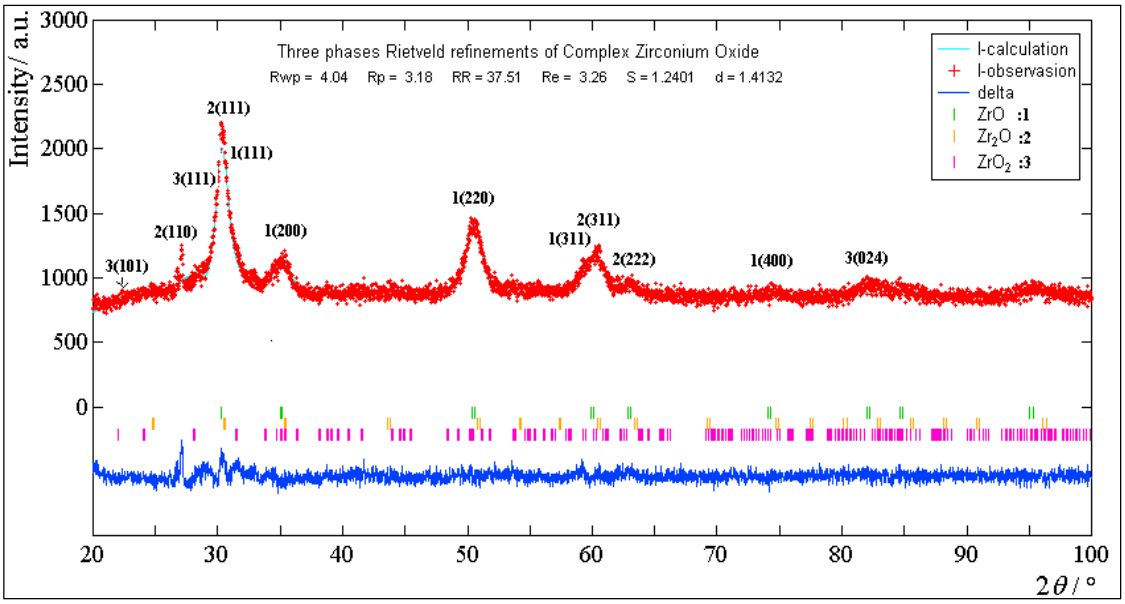


Figure 2 Three phases of complex zirconium oxides diffraction pattern; number in front of every (*hkl*) index indicate the individual phase, in this case 1 representsZrO; 2 represents Zr_2O and 3 represents ZrO_2. The experimental intensity is shown as red dots (•), the refined intensity is shown as a solid line (—) and the peak positions of the three phases are indicated by bars of various colours.

The diffraction pattern consists of three phases, namelyZrO (phase 1), with a face centered cubic crystal structure (fcc), Zr_2O (phase 2), with a cubic primitive crystal structure (p), and phase 3 which is ZrO_2, with an tetragonal crystal structure. The background intensityinitially increases at lower 2θvalues, and then starts to decrease gradually at higher 2θ, which is a strong indication of its thermal vibration origins[8].The results of Rietveld refinement analysis of this sample are tabulated in Table-3.

Table-3.The lattice parameters, density, andfractionresults of the refinement

No	Compounds	Lattice parameters (Å)/ (°)						V(Å^3)	Density	Fraction
		a	b	c	α	β	γ		(gcm^{-3})	(%)
1	ZrO	5,114	5,114	5,114	90,0	90,0	90,0	133,746	5.32496	0.69
2	Zr_2O	5,088	5,088	5,088	90,0	90,0	90,0	131,717	5.00361	40.2
3	ZrO_2	5,210	5,260	5,370	90,0	90,0	90,0	145,157	5.63847	59.12

From the iteration process using the inputs model as shown above, the obtained fractional quantity of ZrO, Zr_2O, and ZrO_2, are 0.69 %, 40.2%, and 59.12% respectively. The refinement results of other structural parameters, such as the isotropic temperature factor and fractional coordinate for each element in the compound are listed in Table-4

Table-4.Additional refined structural parametersresults of the Rietveld analysis methods

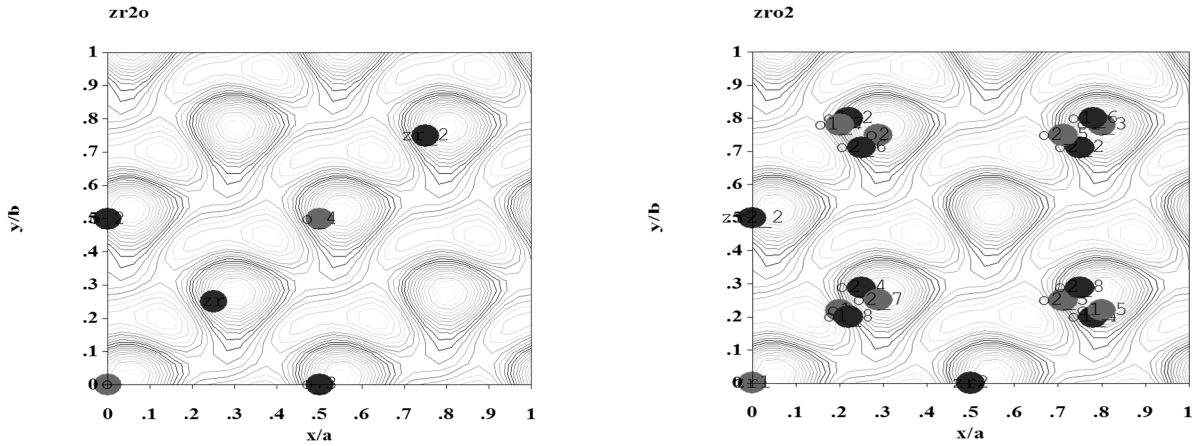
No	Compounds	element	Temperature	Fractional Coordinate (x,y,z,)		
			Factor, B	x	y	z
1	ZrO	Zr	0.578072	0.25	0. 25	0. 25
		O	1.11218	0.00	0.00	0.00
2	Zr_2O	Zr	1.01116	0.25	0. 25	0. 25
		O	1.36589	0.00	0.00	0.00
3	ZrO_2	Zr(1)	$3.50485x10^{-3}$	-0.17537	0.00	0.00
		Zr(2)	2.42993	0.450376	$2.191x10^{-3}$	0.519256
		O(1)	5.82368	0.195833	0.224833	0.268723
		O(2)	9.16378	0.329591	0.711647	0.188996

The refinement reliability factors valuesR_I, R_F, R_{wp}, R_p, $R_E$are tabulated in Table-5.

Table-5.Refinement reliability factors values

No	Compound	R_I	R_F	R_{wp}	R_p	R_E
1	ZrO	4.42	2.89			
2	Zr_2O	5.38	3.62	4.67	3.59	3.25
3	ZrO_2	9.68	5.33			

The Fourier electron density map for the ZrO_2 and the Zr_2O phases in the sampleis shown in Figure 3.



Zr_2O ZrO_2

Figure 3. Fourier electron density map calculated by Fullprof for the ZrO_2 and the Zr_2O phases in the sample in the (001) diffraction plane.Contours are drawn from (21.817 to +27.569)$\times 10^3$ e/Å^3 with an interval of 2.69 10^3 e/Å^3. The Zr and O atoms are shown as solid circles (•) and e is the electronic charge, 1.6022×10^{-19} C.

In figure 3, the electron density map in the (001) diffraction plane based on the X-ray diffraction data is presented as continuous lines (contours) surrounding an atom and is generally not symmetric in shape. As is shown by the Rietveld analysis method, the predominant phases in the alloy are Zr_2O and ZrO_2. In the unit cell, the Zr_2O phase consists of Zr and O atoms located at (0.20,0.220,0.210) for O1 and (0.288, 0.750,0.21) for O2 atoms, (0,0,0) for Zr1 atom and finally (0,0.50,0.50) for Zr2 atom. In the ZrO_2 phase, the O atom is located at (0,0,0) whereas the Zr atom is at (0.25,0.25,0.25). In both phases the contours are primarily directed toward the [010] direction, indicating that the molecular vibration is directed toward the tetrahedral direction, which explains the asymmetric shape of the contours. As is obvious from the maps, some Wyckoff equivalent sites in the ZrO_2tetragonal unit cell are shared by the two atoms, indicating nuclear bond between the the two atoms at certain localized Wyckoff sites. No strong Zr-O covalent bonds are observed in both phases, and in the case of Zr_2O the Zr and O atoms seem to be isolated. The Fourier map of ZrO phase is not shown because Fourier analysis failed to produce any sensible map, a factor attributed to the very small presence of this phase in the sample. Therefore this finding is consistent with the Rietveld refinement results presented in Table-3 that the fractional quantity of the ZrO phase is the smallest.

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