THE USE OF THE RIETVELD METHOD TO STUDY THE PHASE COMPOSITION OF CORDIERITE ($Mg_2Al_4Si_5O_{18}$) CERAMICS PREPARED FROM RICE HUSK SILICA

Wasinton Simanjuntak[1] and Simon Sembiring[2*)]

1. Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Lampung, Lampung 35145, Indonesia
2. Department of Physics, Faculty of Mathematics and Natural Sciences, University of Lampung, Lampung 35145, Indonesia

[*)] *E-mail: sembiring@unila.ac.id*

Abstract

This research presents the use of the Rietveld method to study the phase composition of cordierite ($MG_2AL_4SI_5O_{18}$) ceramics prepared from rice husk silica, after the samples were sintered at 1300, 1400 and 1500 °C. The formation of cordierite is temperature-dependent as indicated by the relative phase composition obtained from x-ray diffraction patterns for the cordierite and spinel increased markedly with increasing temperature, i.e, from 38.98 to 54.15 wt% and from 11.81 to 17.99 wt % following the increase in temperature from 1300-1500 °C, respectively. The above values were obtained with the aid of the Rietveld method, carried out until the goodness of fit values (GoF) reached below 2, which is considered a satisfactory value to reveal the real phase composition. Different plots produced by refinement using the Rietveld method also reveal a reasonable fit between the observed and the calculated plot, demonstrating the usefulness of the method for calculating the quantity of phase composition in the sintering process.

Keywords: cordierite ceramics, rice husk, Rietveld phase analysis, sintering

1. Introduction

Many researchers have been interested in the utilization of rice husk as an excellent source of high-grade amorphous silica [1-3]. In our previous research, active silica from rice husk was obtained by simple acid-leaching, and the structure of silica was found to be amorphous, but could be transformed into crystoballite and trydimite by sintering the sample at temperatures of 700 °C or higher [4]. Due to the high surface area, high grade of amorphous silica, and fine particle size, rice husk has become an important, competitive material for the preparation of various materials including silica ceramics such as cordierite ceramics [5-6], solar grade silicon [7], silica carbide [8], magnesium-alumina-silica [9], and lithium-aluminum-silica [10].

Cordierite ($MG_2AL_4SI_5O_{18}$) is a promising material which has a wide range of uses and applications as substrates in microelectronic applications because of its low dielectric permittivity (ε) = 4 at 1 MHz [11]. Therefore, various techniques, such as slip casting [4], chemical precipitation [5], sol-gel [12], solid-reaction [13] and melting [14] have been investigated in order to decrease sintering temperature of cordierite. The sol-gel process has enabled the production of ceramics material of high purity, homogeneity, and superior properties at lower temperatures than the other techniques. Considerable effort has also been devoted to the study of cordierite as the component of refractory material [15], for its high thermal and chemical stability [16]. In addition, cordierite has a general use in thermal applications because of its low thermal expansion. For example it has been used as a substrate of catalyst for exhaust and gas emissions control in automobile [17], and as support in heat exchangers for gas turbine engines and furnaces [18]. Finally, cordierite is also used as an integrated circuit substrate because of its low dielectric constant i.e, approximately, ε = 5-6 [18-19].

In this paper, the Rietveld method is used to study the phase composition of cordierite ceramics prepared from rice husk followed by sintering at temperatures of 1300, 1400, and 1500 °C. Rietveld method of powder diffraction pattern can illustrate the detailed structure and composition of a polycrystalline sample. A starting model is always used to calculate an entire diffraction pattern, where the model parameters are refined by the method of least squares until a good fit to the observed data is obtained. Qualitative x-ray diffraction analysis was conducted by comparing the diffraction lines with the Standard Powder Diffraction Data Base using search-match procedure. The parameters refined for all samples were those controlling pattern intensity (scale factor), peak profile (width and shape), peak position (zero point and unit cell), and background. The crystal structure models used in the calculation were taken from the Inorganic Crystal Structure Data Base [20]. The refinements were performed by the Rietica program for Windows 95/98/NT version 1.66, and the final Rietveld scale factors were converted to phase composition by weight using the ZMV expression proposed by the Hill and Howard [21].

2. Experiment

Silica from rice husk, ($Mg(NO_3)_2.6H_2O$), and $Al(NO_3)_3.9H_2O$ (merck, kGaA, Damstadt, Germany) were used as raw materials. The Silica sol in this study was obtained following the procedure that has previously been applied [4]. Preparation of *cordierite* ceramics from rice husk using the sol-gel method had previously been conducted, in the following proportion ($Mg(NO_3)_2.6H_2O$) : $Al(NO_3)_3.9H_2O$: SiO_2 sol from rice husk (2:2:5) [5,22]. XRD analysis was used to identify the phases present in the samples. XRD patterns were obtained using an automated Shimadzu XD-610 X-ray diffractometer. The operating conditions used were CuK_α radiation (λ = 0.15418), produced at 40 kV and 30 mA, with a 0.15° receiving slit. Patterns were recorded over goniometer (2θ) ranges from 5-100° with a step size of 0.04 and counting time 1s/step, and using post-diffraction graphite monochromator with a NaI detector.

3. Results and Discussion

Qualitative XRD was conducted by comparing the diffraction lines with the standard PCPDF files using search-match method. Based on our investigations in 2009 [22], a search-match method using PDF file numbers showed that the major phases obtained for the sample without sintering were crystoballite (PDF-39-1425), stishovite (PDF-45-1374) and corundum (PDF-46-1212). Phases of cordierite (PDF-13-0294), crystoballite, spinel (PDF-21-1152) and corundum were obtained for the samples sintered from 1400 to 1500°C as shown in Table 1.

The presence of crystoballite and corundum observed for the sample without sintering, suggests that the raw material does not react to form cordierite, which agrees well with the results obtained by others [23]. The conventional solid state reaction process for formation of cordierite compound is believed to occur through exothermic reaction at temperatures of 1300-1600°C according to the following reactions [23]:

$$SiO_2 + Al_2O_3 \rightarrow Si(OAl)_3(OSi) \quad (1)$$

$$Al_2O_3 + MgO \rightarrow MgAl_2O_4 \quad (2)$$

$$Si(OAl)_3(OSi) + MgAl_2O_4 \rightarrow Mg_2Al_4Si_5O_{18} \quad (3)$$

However, the reaction processes were usually more complex. The peak intensities for cordierite and spinel were found to increase with increased sintering temperatures, but the opposite is true for crystoballite. The most significant result observed is the increased cordierite phase with increased sintering temperatures.

Figure 1 shows the final XRD Rietveld plot for the sample without sintering, while Figure 2, 3 and 4 present the final Rietveld plots for the samples sintered at 1300, 1400 and 1500 °C, respectively. Rietveld analysis was found to provide quantitative information regarding the phases present in the sample, therefore could distinguish the phase composition of the samples sintered at different temperatures, based on the figures-of-merit, as compiled in Table 2. As can be seen, the goodness-of fit (GoF) values were relatively low, i.e all approximately less than 2%, which is considered as acceptable according to basic principle of GoF less than 4% and Rwp less than 20% [24]. In addition, visual results of the plots (Figures 1, 2, 3, and 4) show the accomplishment of the Rietveld refinement, as reflected by small difference between calculated and observed

Table 1. Phase Identification of Sample without Sintering (ws) and Sintered at 1300, 1400 and 1500 °C

Temp (°C)	2θ	Phase
ws	21.6	Crystoballite
	31.3	Stishovite
	35.4	Corundum
1300	10.3	Cordierite
	21.5	Crystoballite
	21.3	Silica
	29.9	Spinel
	30.3	Rutile
	36.3	Corundum
	29.1	Candialite
1400	10.3	Cordierite
	21.5	Crystoballite
	21.3	Silica
	29.9	Spinel
	35.4	Corundum
1500	10.3	Cordierite
	21.5	Crystoballite
	29.9	Spinel
	35.4	Corundum

Table 2. Figures-of Merit from Rietveld Refinement with XRD Data for the Samples without Sintering (ws) and at Temperatures of 1300, 1400 and 1500 °C for 3 Hours

Temp (°C)	R_{exp}	R_{wp}	GoF
ws	12.60	15.22	1.7
1300	9.12	12.52	1.8
1400	10.42	17.84	1.6
1500	9.47	16.40	1.5

Table 3. Relative Phase Composition (wt%) from Rietveld Refinement with XRD Data for the Samples without Sintering and at Temperatures of 1300, 1400 and 1500 °C for 3 Hours

Temp (°C)	C	CR	SI	ST	SP	CD	CA	RU
Ws	-	40.46	-	11.02	-	48.52	-	-
1300	38.98	28.25	9.12	-	11.81	18.22	0.01	3.62
1400	39.64	26.51	10.28	-	12.44	12.13	-	-
1500	54.15	20.80	-	-	17.99	9.06	-	-

C = Cordierite; CR = Crystoballite; SI = Silica; ST = Stishovite; SP = Spinel; CD = Corundum; CA = Candialite; RU = Rutile

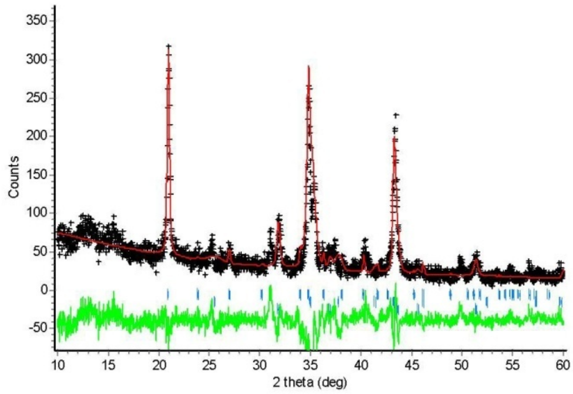

Figure 1. XRD Rietveld Plot for the Sample without Sintering. The Observed Data are Shown by the (+) Sign, and the Calculated Data by a Solid Line (red). The Vertical Line Represents the Point Series hkl. The Green Line Below the Vertical Lines is the Difference Profile

patterns. The RB factors for each phase in each refinement with XRD data were approximately 2.42-14.93% for cordierite, 2.42-14.46% for crystoballite, 6.14-5.31% for silica, 4.28% for stishovite, 9.35-3.08 for spinel, 2.61-17.61 for corundum, 4.54% for candialite and 5.12% for rutile.

Table 3 shows the relative phase composition (wt%) of the sample without sintering and those sintered at 1300, 1400 and 1500 °C from the XRD data. The relative phase compositions obtained from XRD patterns for the cordierite phase increased markedly with increasing temperature, *i.e* from 38.98 wt% at 1300 °C to 54.15 wt% at 1500 °C. The wt% of crystoballite decreased from 40.46 to 20.80 with increased temperature up to 1500 °C. The wt% of spinel increased markedly from 11.81-17.99% as a result of increased temperature from 1300 to 1500 °C.

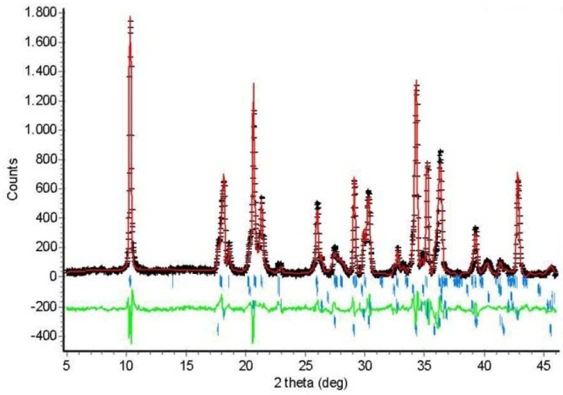

Figure 2. XRD Rietveld Plot for the Sample Sintering at 1300 °C. The Observed Data are Shown by the (+) Sign, and the Calculated Data by a Solid Line (Red). The Vertical Line Represents the Point Series hkl. The Green Line Below the Vertical Lines is the Difference Profile

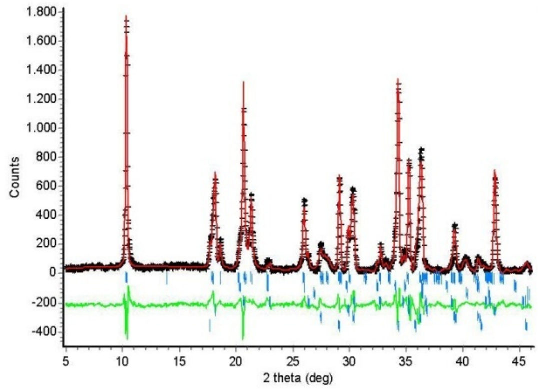

Figure 3. XRD Rietveld Plot for the Sample Sintering at 1400 °C. The Observed Data are Shown by the (+) Sign, and the Calculated Data by a Solid Line (red). The Vertical Line (Blue) Represents the Point Series hkl. The Green Line Below the Vertical Lines is the Difference Profile

4. Conclusion

The quantitative phase composition of cordierite prepared from rice husk silica by the Rietveld technique with XRD data has been well demonstrated, confirming that the formation of cordierite is temperature dependent. XRD results show that the cordierite phase increased with increased temperature, and the Rietveld analysis results showed that the GoF values obtained satisfy the required values of ≤ 4. Also, the fluctuation in the different plots shows a reasonable fit between the observed and the calculated plots.

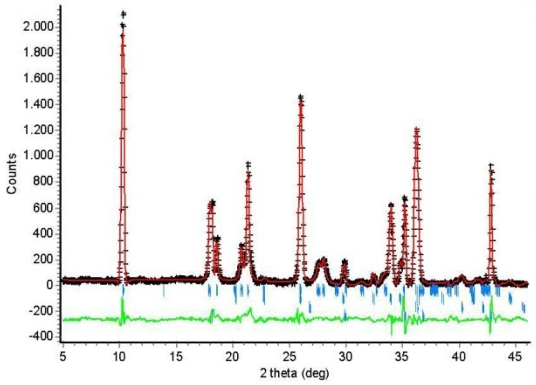

Figure 4. XRD Rietveld Plot for the Sample Sintering at 1500 °C. The Observed Data are Shown by the (+) Sign, and the Calculated Data by a Solid Line. The Vertical Line (Blue) Represents the Point Series hkl. The Green Line Below the Vertical Lines is the Difference Profile

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