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# Rietveld analysis of geopolymer prepared from amorphous rice husk silica with different thermal treatment

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**Abstract.** The work aims to study the temperature effect on the geopolymer's crystal structure prepared from amorphous silica rice husk. The samples were prepared via the sol-gel method and then subjected to thermal at a temperature of 250-650 °C. EDS identified the element and compound composition on the surface of the sample. The crystal structure of samples identified by Rietveld refinement of XRD. The sample was dominated by the gibbsite phase at relatively low temperatures (250 °C). The boehmite phase dominates at a temperature of 350-450 °C. The amorphous structure of the geopolymer was formed at a temperature of 550-650 °C. The geopolymer mainly formed from the reaction of boehmite and silica. This study shows a significant effect of temperature on the formation of the geopolymer structure.

## 1. Introduction

Geopolymer is an inorganic aluminosilicate polymer which formed mainly by polymerization reaction between alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ )[1]. The geopolymer structure consists of  $[\text{AlO}_4]$  and  $[\text{SiO}_4]$  tetrahedral linked by sharing all oxygen atoms in a three-dimensional network called polysialate chains[2]. The linkages of  $[\text{AlO}_4]$  and  $[\text{SiO}_4]$  tetrahedral require cations such as  $\text{Na}^+$ ,  $\text{K}^+$ , or  $\text{Li}^+$  to balance the negative charge of aluminum elements located in tetrahedral coordination of the network[3]. Geopolymer has an amorphous or semicrystalline structure[4], high specific surface area, and porosity[5]-[7], but the material exhibits excellent mechanical properties[8]-[9]. Previous studies revealed that a geopolymer has an ionic electrical resistivity of about  $0.67 \times 10^6 \Omega \cdot \text{cm}$  at room temperature and frequency of 200 kHz[10], low capacitance[11], low relative permittivity[12], excellent thermal resistance, and good chemical resistance[2]. These properties make it is very suitable for ionic conductor material, which can be applied as an element of a solid-state battery or electrochemical sensor, and so on[10].

Geopolymer is usually produced from the geopolymerization process[13]. Through this process, a geopolymer is prepared by activating raw materials using high concentrated alkaline solutions and followed by curing treatment[14]-[16]. The raw materials commonly used are generally waste materials or natural resources, which primarily containing aluminosilicate compounds such as fly ash[17]-[19], slag[20], clay[21]-[23], kaolin[5], and metakaolin[24]-[25]. This process's advantage is that a geopolymer structure can be obtained by curing treatment at low temperatures under atmospheric pressure. However, the process must be taken a long time[26]-[29]. Furthermore, high



purity geopolymer is challenging to obtain because chemical compositions of raw materials are very complex; thus, geopolymer resulting from this process always accompanied by secondary phases such as quartz, albite, mullite, hematite, or maghemite[20]-[21], [30]-[33]. In addition to the geopolymerization process, the sol-gel method can be applied to synthesize a geopolymer. The technique offers homogeneity and prevention of phase segregation during the heating process to obtain high purity geopolymer [10],[12]. For example, Zheng et al. (2009)[34] obtained high purity geopolymer using sol-gel by reacting tetraethoxysilane (TEOS) and aluminum nitrate as starting materials. They reported that the geopolymer obtained from this process shows high purity, although at high-temperature calcination of about 300-800 °C.

In the context of silicate materials development, including geopolymer, silica is an essential element, and it can be produced from rice husk. This agricultural waste is known to have high purity amorphous silica content of more than 98 %, extracted by a simple method and low-cost[35]-[36]. Several research types applied the acid leaching method to obtain amorphous silica[37]-[38]. This method is based on rice husk amorphous silica solubility, which is very low at pH<10 and increases significantly at pH >10. This characteristic makes the amorphous silica extracted from rice husk by solubilizing under alkaline solution followed by precipitating at a lower pH[39]. Amorphous silica from rice husk has been used to synthesize various materials. In our previous studies, it has been successfully utilized as raw material to produce high purity ceramic materials, such as cordierite[40]-[42], forsterite[43], and sodium ferrosilicate[44].

Previously, we produce geopolymer samples from amorphous rice husk silica and sodium aluminate solutions. We find qualitatively that the phases are dominated by gibbsite, boehmite, and amorphous geopolymer at low, middle, and high temperatures[45]. In this study, we continue the study with the Rietveld analysis to determine the phase qualitatively. This work aims to evaluate the thermal effect of the sample's crystal structure. The samples were subjected to thermal at 250-650 °C and then characterized by using energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD).

## 2. Materials and methods

The chemicals used in this study consist of gibbsite ( $\text{Al}(\text{OH})_3$ ) and  $\text{Na}(\text{OH})$  purchased from Merck,  $\text{HNO}_3$  (68 %) obtained from Chemical Product, and silica sol extracted from rice husk. This study's types of equipment consist of EDS (JEOL JSM-6360LA) and XRD (Shimadzu XTD-7000 Maxima X).

### 2.1 Preparation of rice husk silica sol and sodium aluminate sol

Rice husk silica sol was obtained using a method reported in our previous studies[40]-[44]. In the first step, 50 g of rice husk and 500 ml of  $\text{NaOH}$  (5%) were mixed in a beaker glass followed by boiling for 30 minutes. In the second step, the extract solution was filtered to separate the silica sol from the remaining rice husk. In the last step, the silica sol was cooled at room temperature for 24 hours. Meanwhile, sodium aluminate sol was prepared by dissolving 5 g of gibbsite ( $\text{Al}(\text{OH})_3$ ) into 50 ml of  $\text{NaOH}$  under magnetic stirring with the rate of 500 rpm for 2 hours to obtain homogeneous sodium silicate sol.

### 2.2 Geopolymer preparation

Geopolymer preparation was conducted by mixing rice husk silica sol and sodium aluminate sol with a volume ratio of 5:1. The mixture was stirred under a magnetic stirring of 1000 rpm at room temperatures for 5 hours. The mixture's acidity was set by dropwise addition of 5 %  $\text{HNO}_3$  solution under stirring until it has a pH of 7. The mixture obtained from this process was filtered until geopolymer gel was obtained. The pre-calcination treatment at 110 °C was applied to the gel for 7 hours until the solid geopolymer precursor was obtained. The precursor was sieved to get a powder with a maximum particle size of 100  $\mu\text{m}$ . The powder was subjected to a temperature at 250–650 °C

using temperature-programmed with constant heating rate 5 °C/min and holding time of 3 hours at peak temperature.

### 2.3 Energy-dispersive spectroscopy (EDS) analysis

The sample was characterized by using EDS (JEOL JSM-6360LA) to evaluate the elements or compounds on the sample's surface. We analyzed only sample calcined at 250 °C to characterize because all samples were made in the same composition.

### 2.4 Rietveld analysis

The samples were characterized by an x-ray diffractometer (Shimadzu XTD-7000 Maxima X) with  $\text{CuK}\alpha$  radiations with wavelength  $\lambda = 0.15418 \text{ \AA}$ . The diffractogram was recorded over the goniometry ( $2\theta$ ) ranging from  $10^\circ$ - $80^\circ$  with step size 0.02 and counting time 1 sec/step. The crystal structure analysis was conducted qualitatively using QualX2.0 software[46], and Rietveld refinement analysis by using Rietica software.

## 3. Result and discussion

The EDS spectrum of the geopolymer sample is displayed in Figure 1. The spectrum exhibits the presence of some elements such as sodium (Na), aluminum (Al), silicon (Si), and oxygen (O) with mass percentages of 0.95 %, 18.59 %, 29.73 %, and 50.73 %, respectively. In the form of oxide compounds, the sample is composed of  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$ . Mass percentages of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Na}_2\text{O}$  are 63.60 %, 35.13 %, and 1.27 %, respectively. This analysis indicates that several elements or compounds needed to form the geopolymer structure are available in the sample because they are constructed from combining the compounds. The compounds' presence allows the formation of high purity geopolymer because there are no impurity elements or compounds that appear in the sample.

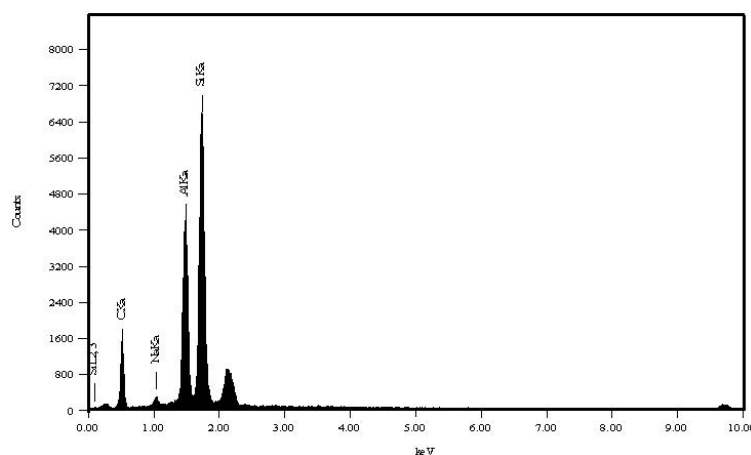
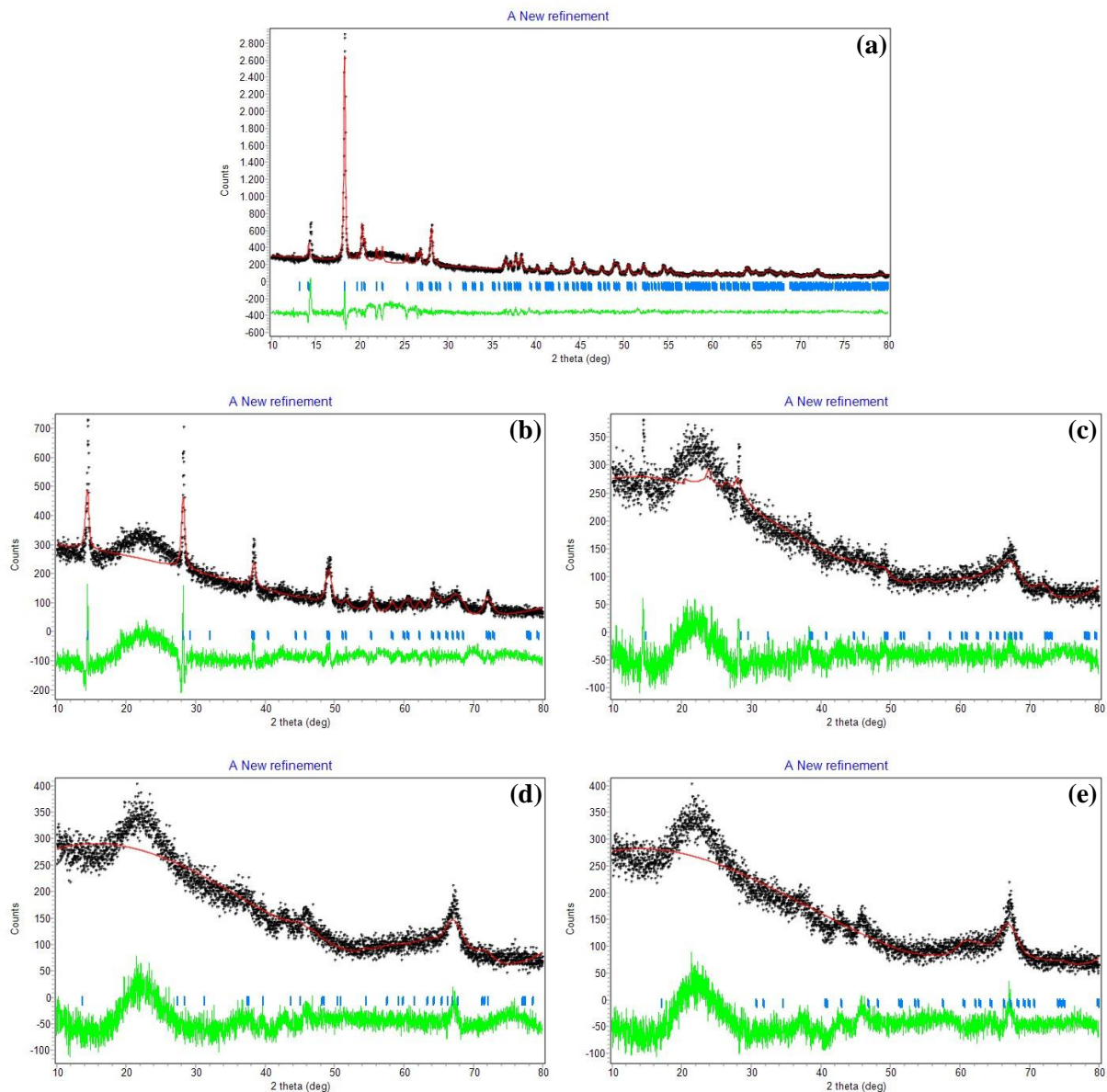


Figure 1. EDS spectrum of geopolymer

Table 1. Rietveld refinement parameters of geopolymer samples

Heating temperature (°C)	$R_{\text{exp}}$	$R_{\text{wp}}$	$R_{\text{p}}$	$GoF$
250	7.54	14.01	10.53	3.453
350	7.75	15.00	12.23	3.746
450	7.82	12.04	9.67	2.369
550	7.67	11.83	9.55	2.377
650	7.79	12.83	10.35	2.710



**Figure 2.** Rietveld refinement of XRD pattern of geopolymer which subjected to heat with different temperature, (a) 250 °C, (b) 350 °C, (c) 450 °C, (d) 550 °C, and (e) 650 °C

Based on the results of the qualitative analysis using QualX software via search-match, the sample which subjected to thermal at the temperature of 250 °C match with the database of the gibbsite phase ( $\text{Al}(\text{OH})_3$ ). Samples subjected to thermal at temperatures of 350-450 °C good agreement with the boehmite ( $\text{AlOOH}$ ) phase database. Meanwhile, the sample subjected to thermal at temperatures of 550-650 °C was dominated by the amorphous phase, but several peaks match the boehmite phase. This qualitative analysis is used for a qualitative analysis (Rietveld refinement) using the Rietica software. The results of the Rietveld refinement XRD pattern of the samples are depicted in Figure 2. The refinement results include all samples show that the goodness of fit (GoF) value required by Rietveld's analysis, which is less than 4 and  $R_{wp}$  less than 20[47]-[48], as shown in Table 1.

The Rietveld refinement of the sample subjected to thermal at 250 °C (Figure 2(a)) represents the high crystalline structure. Figure 2(a) clearly shows that the sample is the gibbsite based on the refinement results. The refinement confirmed that the sample has a monoclinic structure with space group  $P21/n$ . The phase of the sample treated thermally at 350 °C also exhibits a high crystalline structure (Figure 2(b)), but the phase is different from the sample subjected to thermal at 250 °C. The refinement results clearly show that it is a boehmite (AlOOH), an orthorhombic structure, and a space group of  $Amam$ . Cell parameters for both samples show in Table 2. The phase transformation from gibbsite to boehmite causes significant changes in cell parameters and volume. The gibbsite and boehmite domination in the samples subjected to thermal at 250-350 °C indicates no polymerization reaction between the raw materials used to produce a geopolymer. The domination of gibbsite and boehmite phases in the temperature range is due to gibbsite, which initially from raw material requires the lower temperature to grow to be a crystal. Otherwise, silica needs a higher temperature to achieve a crystalline state.

**Table 2.** Cell parameters geopolymer samples

Heating temperature (°C)	Phase	Crystal structure	Space group	a (Å)	b (Å)	c (Å)	Cell volume (Å <sup>3</sup> )
250	Gibbsite	Monoclinic	$P21/n$	8.6590	5.0770	9.7030	425.42
350	Boehmite	Orthorhombic	$Amam$	3.7000	12.2270	2.8680	129.75
450	Boehmite	Orthorhombic	$Amam$	3.7000	12.2270	2.8680	129.75
550	Boehmite	Orthorhombic	$Amam$	3.7000	12.2270	2.8680	129.75
650	Boehmite	Orthorhombic	$Amam$	3.7000	12.2270	2.8680	129.75

Based on the refinement results, the sample thermally treated at 450 °C still has the same phase as the sample thermally treated at 350 °C, i.e., the boehmite phase with orthorhombic structure and  $Amam$ 's space group with cell parameter as shown in Table 2. Nevertheless, the diffractogram changes, as depicted in Figure 2(c) characterized by a decrease in intensity of the peaks at an angle of  $2\theta = 14.49^\circ$  and  $28.18^\circ$ , which are the primary and secondary peaks of the boehmite phase, respectively. Besides, at this angle range, a broad peak is created, which characterizes the amorphous silica phase in the sample. These changes indicate that the sample is beginning to undergo a polymerization process to form a geopolymer structure. Significant changes occurred in the thermally treated samples at 550-650 °C, as shown in Figures 2(d)-(e). Even though, according to the refinement results, the sample still has a boehmite phase with an orthorhombic structure with a cell parameter as shown in Table 2, the primary and secondary diffraction peaks that characterize this phase have disappeared. Besides, the two samples' diffractograms tend to show that the phase contained therein is amorphous. Based on the previous report, the amorphous phase formation shows a strong indication of geopolymers' formation in both samples[4],[47]. These refinement results show a significant role of temperature in the formation of geopolymer structures. From this study, it is concluded that the geopolymer based on silica of rice husk is formed from the reaction of the boehmite and silica phases under high-temperature conditions.

#### 4. Conclusion

This study's results indicate that heat treatment strongly influences the phase and crystal structure of each sample. At a temperature of 250 °C, the sample is a gibbsite phase with a monoclinic structure. It grows to be a boehmite phase with an orthorhombic structure at a temperature of 350-450 °C. Meanwhile, the geopolymer structure is formed in the temperature 550-650 °C.

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