SYNTHESIS AND CHARATERISATION OF RICE HUSK SILICA BASED BOROSILICATE (B$_2$SiO$_5$) CERAMIC BY *SOL-GEL* ROUTES

Simon Sembiring

Material Research Group, Department of Physics, Faculty of Mathematics and Natural Science, Lampung University
Jl. Prof. Soemantri Brojonegoro No.1, Bandar Lampung

ABSTRACT

In this research, borosilicate ceramics were produced from rice husk silica. Preparation of borosilicate ceramics was conducted by mixing boron oxide sol from borax with silica sol extracted from rice husk. The boron oxide was produced by hydrolysis of borax using H$_2$SO$_4$ 5%. The samples were synthesized with different compositions, with the ratios of silica to boron oxide are 8:1, 8:2, 8:3 and 8:4. The samples were sintered at 900 °C. Functional groups were examined using FTIR spectroscopic technique. Structural and microstructural characteristics were examined by XRD and SEM, respectively. The chemical resistance of borosilicate is evaluated by gravimetric method using H$_2$SO$_4$, HCl, NaOH and KOH. The FTIR study revealed that the main functional groups are Si-O-Si, B-O-B, and B-O-Si. The x-ray diffraction (XRD) study revealed that the main crystalline phases are borosilicate (B$_2$SiO$_5$) and boron oxide (B$_2$O$_3$). SEM investigations clearly demonstrated that the smaller particle size was found with increasing in boron oxide concentration. From the chemical resistance test carried out, it was obtained that the produced borosilicate possessed high resistance to acids and alkalis.

INTRODUCTION

Borosilicate (B$_2$SiO$_5$) glass or ceramic composite is one of the promising material which has a wide range of applications because of its low thermal expansion [1], superior chemical resistance [2], and low dielectric constant *i.e*, approximately, ε = 4.8 at 1 MHz [3]. For these reasons, borosilicate is widely used as laboratory glassware, industrial piping, bulbs for hot lamps and electronic tubes. Besides these applications, borosilicate also plays an important role in the production of vycor glass at low-working temperature. The performance of borosilicate strongly depends on the structure and microstructure. As an example, the presence of crystoballite structure on the borosilicate was reported to enhance dielectric constant and thermal expansion coefficient [3]. In addition, decreasing borosilicate sintering temperatures is also important for circuit material, since higher temperatures would cause the circuit materials to be oxidized. Therefore, in order to decrease sintering temperature, various techniques have been used to fabricate borosilicate, such as slip casting [4], chemical precipitation [5], sol-gel [6-7], and melting [8]. The sol-gel process enables the production of ceramics material of high purity, homogeneity and superior properties at lower temperature than the other techniques. Considerable effort has also been devoted to the study of borosilicate as component of refractory material [7] for its high thermal and chemical stability. In

addition, borosilicate has a general use in thermal application because of its low thermal expansion, approximately 3.3 10^{-6}/°C [9], *i.e.* element of filament for x-ray instrument [10], support in heat exchangers for gas turbine engines and furnaces [1]. Moreover, borosilicate is also used as an integrated circuit substrate because of its low dielectric constant [3].

Rice husk has become an important and competitive material for preparation of various materials. Many researchers have concluded that rice husk is an excellent source of high-grade amorphous silica [11-14]. Utilization of rice husk as a source of silica is based on removal of impurities with low cost and production of silica with high specific surface area. In the previous investigations, several researchers have shown that reasonably pure silica can be obtained from rice husk by a simple acid-leaching method [12,15]. It has also been reported that active silica from rice husk could be produced by using KOH 5% [16], and the structure of silica obtained was amorphous but could be transformed into crystoballite and trydimite by sintering of the sample at temperature ranging from 700–900 °C [17]. Due to the high surface area, high grade of amorphous silica, and fine particle size, rice husk silica has been shown to be a good material for the preparation and synthesis of various materials such as, pure silicon [15], solar grade silicon [18], cordierite [19-22], silica nitride [23], silica carbide [24], magnesium-silica [25], and lithium-aluminum-silica

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* Corresponding author. Tel/Fax : +62-721-704625/704625
Email address : sembiring@unila.ac.id

[26]. In the present study, utilization of rice husk silica as a raw material for synthesizing borosilicate is also intended to create value added from rice farming. This study focuses on the synthesis and characterization of rice husk silica based borosilicate ceramic by sol-gel routes. The borosilicate ceramic was synthesized from rice husk silica and other water-based precursor materials following a simple step wet-chemical process. The borosilicate synthesized was characterized by functional group analysis (FTIR), structure (XRD), microstructure (SEM) and chemical resistance to acids and alkalis.

EXPERIMENTAL SECTION

Materials

Raw materials used for the experiments were rice husk as sources of silica and borax [$(Na_2)B_4O_7.10H_2O$] as sources of boron oxide, respectively. Other chemicals used were KOH 5%, H_2SO_4 5%, HCl 5%, NaOH 5%, distilled water, pH indicator, and filter paper.

Instrumentation

The equipments used in this study are a Perkin Elmer FTIR, an automated Shimadzu XD-610 X-ray diffractometer with CuK_α radiation (λ = 0.15418), produced at 40 kV and 30 mA, a Philips-XL scanning electron microscopy (SEM), and a microbalance Mettler Instrument AG, CH-8806 Greifensee-Zurich.

Procedure

Synthesis of borosilicate powders using the sol-gel method was performed in three steps, (i) preparation of silica and boron sols, (ii) preparation of borosilicate with various ratios of silica to boron oxide, and (iii) characterization and chemical resistance tests.

Preparation of silica and boron sols

Preparation of silica sol was conducted following the procedures that have previously been applied [13,16]. In the first step, rice husk was washed with hot water to remove contaminants of water soluble organic matters present, and then dried in the room temperature. The dried husk (50 g) were stirred in 500 mL of 5% KOH solution. The mixture was boiled in a baker glass for 30 min. The mixture was allowed to cool to room temperature and left for 24 h. The mixture was filtered to separate the filtrate which contains silica (silica sol). Boron sol was prepared by dissolving 100 g of borax into 500 mL solution of H_2SO_4 5%. The borax solution was stirred in a beaker glass for 8 h.

Fig 1. The pellets of borosilicate sintered at 900 °C
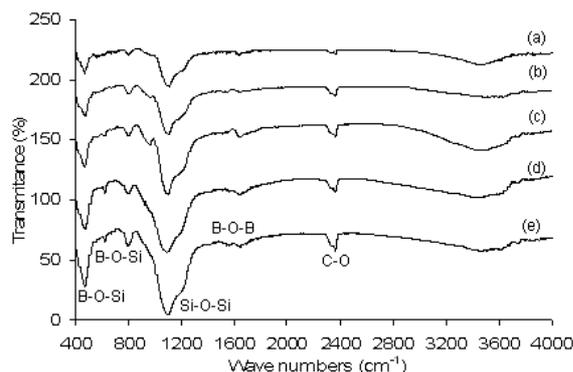
Fig 2. FTIR spectra of borosilicate samples with various boron oxide concentrations after sintered at 900 °C (a) 8:1, (b) 8:2, (c) 8:3 (d) 8:4 and (e) 8:5. The absorption peaks are assigned to functional groups of B-O-Si, B-O-B, Si-O-Si, and C-O

Preparation of borosilicate ceramic

To obtain the solid borosilicate, calculated quantities of silica sol were added under stirring to the appropriate volume of boron sol to give the ratios of silica and boron oxide as a mass ratio of 8:1, 8:2, 8:3 and 8:4. The mixture was heated at 90 °C under continuous stirring to transform the sample (sol) into gel. The gel was dried at 110 °C for 5 h and grounded into powder with the size of 125 μm. The powder was pressed in a metal die with the pressure of 3 ton to produce cylindrical pellet, and then the pellet was sintered at 900 °C (Fig. 1).

Characterization

A Perkin Elmer FTIR was used for the investigation of functional groups of the borosilicate. The sample was mixed with KBr of spectroscopy grade, and scanned in the spectral range of 4000–400 cm^{-1}. XRD patterns were obtained using an automated Shimadzu XD-610 X-ray diffractometer with CuK_α radiation (λ = 0.15418), produced at 40 kV and 30 mA. The patterns were recorded over the goniometer (2θ) ranging from 5°–100° with a step size of 0.04 and counting time 1s/step, and post-diffraction graphite monochromator with NaI detector. Microstructural analysis was conducted using scanning electron microscopy (SEM) Philips-XL, on polished and thermally-etched samples. The chemical resistance of

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the samples was determined for the amount of weight reduction after being kept 24 h at 25 °C in three replicates, using H_2SO_4, HCl, NaOH and KOH at concentration of 10%.

RESULT AND DISCUSSION

Characterization with FTIR

The FTIR spectra of all samples scanned over the wave number range of 4000 to 400 cm^{-1} are compiled in Fig. 2, showing the functionality of the samples with various boron oxide contents, after sintered at 900 °C. Several absorption bands are observed at the wave numbers of 2361, 1624, 1095, 793, 618, and 467 cm^{-1}. The strong peak in the range 1095–1092 cm^{-1} is assigned to stretching vibration of silica, corresponding to the specific structural of siloxane bond Si-O-Si due to the deformation of Si-O bond, as has been observed by others [27-28]. In addition, two the significant absorption peaks at 467 and 793 cm^{-1} were observed, which were commonly attributed to the symmetric and asymmetric stretching vibrations of B-O-Si, due to the incorporation of boron atoms and vibration of tetrahedral SiO_4 entity B(OSi) [29-30]. The shoulder peak at the range of 618–630 cm^{-1} was assigned to the extensive asymmetric stretching vibration of B-O-B. The formation of B-O-B on the surface indicates the transformation of borax to boron oxide. In previous analyses [31-34] it is suggested that B-O-B bond occurs through the stretching vibration of tetrahedral BO_4, after sintered at 900 °C. Beside that, vibration band in the range of 1616–1624 cm^{-1} suggests the presence of O-H bond, associated with bending vibration of the water molecules trapped in the matrix of the silica [7,20,35]. In addition, vibration band of C-O appeared around 2361 cm^{-1} is considered as related to residual carbon from organic components such as cellulose, of the rice husk [35-37].

Characterization with XRD

To gain information on structure development, the samples were analyzed using XRD technique. The phases were identified with the PDF diffraction pattern database (1997), published by the International Centre for Diffraction Data (ICDD) [38], comparing the diffraction lines with the standard PCPDF files using search-match method. The XRD patterns for all samples are shown in Fig. 3. As expected, the XRD pattern of the samples indicated the presence of borosilicate (B_2SiO_5)-PDF-42-0382 and boron oxide (B_2O_3)-(PDF-44-1085), with the most intense peaks observed at $2\theta = 23.16°$ and $2\theta = 31.92°$. The existence of these two phases is also supported by the FTIR results, which confirm the presence of Si-O-B and B-O-B functional groups. As can
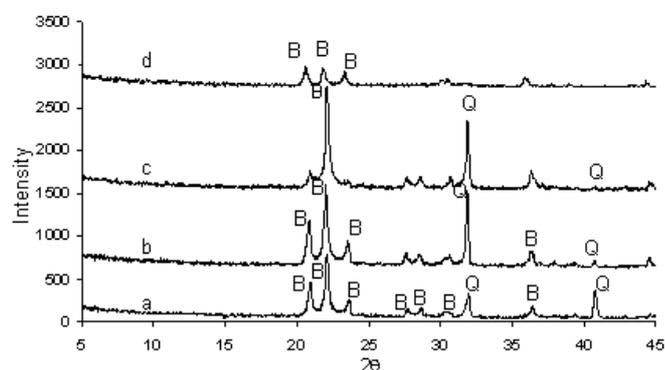
Fig 3. XRD pattern of borosilicate samples with various boron oxide concentrations after sintered at 900 °C, (a) 8:1, (b) 8:2, (c) 8:3 (d) 8:4 using CuK_α radiation (λ = 1.5048 Å). The peaks are labeled B for borosilicate (PDF-42-0382) and Q for boron oxide (PDF-44-1085)
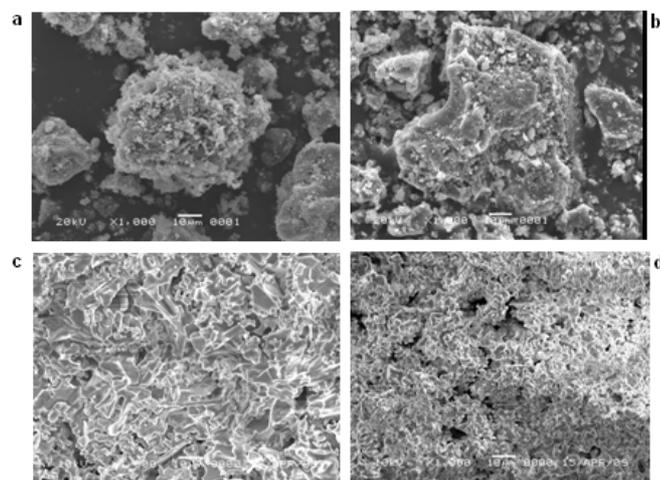
Fig 4. SEM images of borosilicate samples with various boron oxide concentrations after sintered at 900 °C, (a) 8:1, (b) 8:2, (c) 8:3 (d) 8:4

be seen in Fig. 3, the borosilicate was detected in all of the sintered samples. This finding implies that the reaction between tetrahedral of SiO_4 and BO_4 to produce borosilicate took place at temperatures applied, which is in agreement with the results previously reported [10,30,39-40].

An interesting result is the effect of composition on the fate of boron oxide. As can be seen, in the samples with the compositions up to 8:3, the boron oxide phase was well detected. However, in the sample with the composition of 8:4, no boron oxide phase was found. The disappearance of this phase is most likely due to the domination of the borosilicate phase on the surface of the sample, and therefore covered the boron oxide phase, probably present in the inner surface of the sample. This suggestion is supported by the results of SEM analyses described in the following section.

Table 1. Weight loss of borosilicate samples in acids and alkalis

Sample composition	Weight loss in % (mass)			
	H_2SO_4	HCl	NaOH	KOH
8 : 1	0.4531 ± 0.90	0.6117 ± 0.66	0.1812 ± 2.25	0.3398 ± 1.20
8 : 2	0.3775 ± 1.52	0.5664 ± 0.72	0.1132 ± 3.60	0.2945 ± 1.38
8 : 3	0.3096 ± 1.31	0.4531 ± 0.90	0.0830 ± 4.89	0.1887 ± 2.16
8 : 4	0.2189 ± 1.86	0.3851 ± 1.05	0.0704 ± 5.79	0.1585 ± 2.57

Characterization with SEM

To evaluate the surface morphology, the samples were further characterized using SEM. The micrographs of the samples with different composition are shown in Fig. 4 a-d, respectively. The surface morphology of the samples is highly influenced by the boron oxide content. As can be seen, increased content of boron oxide was found to result in more homogeneous surface marked by smaller particle size and more evident grain boundary. In the two first samples (Fig. 4a and 4b), the presence of clusters was clearly observed, indicating that the surface is highly heterogeneous, most likely with localized distribution of the borosilicate and boron oxide on the surface.

In the sample with the composition of 8:3 (Fig. 4c), the feature observed indicates the homogeneous surface with homogeneous distribution of both phases, and therefore, the two phases were detected using XRD technique as previously mentioned. In the last sample (Fig. 4d) the homogeneous surface is also observed, however with smaller particles sizes than those observed in the sample of 8:3 compositions (Fig. 4c). Apart from this similarity, the two samples also displayed a significant different regarding the existence of the boron oxide. As previously mentioned, in the last sample, no boron oxide was detected according to the XRD technique. Combining the XRD and SEM results lead to the conclusion that the surface of the last sample (silica to boron oxide with the ratio of 8:4) is fully covered by the borosilicate phase and therefore hinders the detection of boron oxide using the XRD method.

Chemical Resistance Evaluation

Another characterization of the samples carried out in this study is chemical resistance testing toward acids and alkalis. The resistance was defined in term of weight loss at pressed in % by mass, after the samples were subjected to the acids and alkalis. The average results form three replicate experiments are presented in Table 1, together with standard deviation of the measurements.

As can be seen in Table 1, the weight loss of the samples decreases with increasing boron oxide content in both acids and alkalis solution. With respect to these results, it is concluded that the higher the content of boron oxide, the better the resistance of the sample toward acids and alkalis. It is also observed that the weight loss in alkali (NaOH and KOH) is lower than that in acid (H_2SO_4 and HCl), suggesting that the borosilicate synthesized are more resistance to alkalis.

CONCLUSION

In this paper, synthesis and characterization of borosilicate prepared using rice husk silica and borax were investigated. The results obtained clearly demonstrate that borosilicate ceramic could be produced using rice husk silica and borax as raw material. On the basis of FTIR analyses, reaction between silica and boron oxide to produce borosilicate was confirmed by the presence of Si-O-Si, B-O-B, and B-O-Si functional groups. X-ray diffraction analysis revealed the presence of borosilicate (B_2SiO_5) and Boron oxide (B_2O_3) phases in the ratio of silica and boon oxide at 8:1, 8;2, 8:3, but only borosilicate (B_2SiO_5) phase for 8:4. An irregular and agglomerated morphology of the particles were observed by SEM for 8:1 and 8:2 samples, and small size distribution of the particle was found for the 8:3 and 8:4 samples. It was also found that borosilicate ceramic has high chemical resistance toward acids and alkalis.

ACKNOWLEDGEMENT

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